The TREND IN ENGINEERING

at the University of Washington

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X-RAY SPECTROSCOPIC ANALYSIS OF A SLAG-METAL SYSTEM

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April, 1959

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THE ENGINEERING EXPERIMENT STATION

THE ART OF EXPANDING MINERAL RESOURCES

A Guest Editorial

DRURY A. PIFER
Director of the School of Mineral Engineering

THE WISE USE of the natural resources available to us has profound effects in many fields which we consider vital to our well being. Minerals constitute the great bulk of commodities in the trade and transportation of raw materials and from this it may be concluded that they constitute the most important resource used by man after satisfying the basic need for food and shelter. The availability of minerals (with the products made from them) directly determines the standard of living, which is a measure of consumption; it determines the industrial potential of nations as this rests on the availability of industrial energy and on the existence of raw materials to manufacture; the military strength of a nation is dependent on manufacturing capacity and on the availability of mineral products which constitute seventy-five per cent of munition needs. A most important corollary to mineral availability is that the localization of mineral deposits within the political boundaries or within the trading province of a nation determines the potential standard of living of its citizens and all that this implies with respect to creature comfort, cultural achievement and intellectual activity. In a word, minerals are the material base of modern living. It, therefore, behooves us to use these limited materials most efficiently.

Mineral deposits have unique characteristics which determine their availability and limit their use. First, it is recognized that they are unequally distributed around the globe and that most minerals are a geologic phenomenon of extremely local occurrence. Even continents do not have deposits of all minerals, much less do nations, and the deposits they do possess vary widely in size and quality. Thus, trade is essential to provide some degree of equitable availability. Neither of the great mineral provinces of Europe and North America has the entire range of mineral deposits essential to its industrial economy. Competition, tensions, disagreements, treaties, economic penetrations, are the natural outcome of this difference in mineral potential.

Another factor is that each mineral deposit is limited in extent and its exhaustion demands that a new source of supply be discovered and opened for exploitation. The surface of the earth, even in remote regions, has been well traversed and easily discovered deposits of readily recognized minerals are just about exhausted. The day of the old time prospector has passed. Discovery of significant deposits now rests on systematic exploration by teams of scientists, engineers, and financiers, and even of diplomats representing governments, each contributing essential elements to the effort. Enormous sums of money and much physical and mental effort are expended without assurance of return, but, when success is achieved, the rewards are often spectacular and fully as satisfying to the participants as were the discoveries of the miners of yesteryear.

Modern exploration techniques are by no means applicable to all types of mineral deposits and may even overlook those to which they are applicable. One of the pressing needs of the industry is improvement in existing geophysical methods. New techniques, higher reliability, more precise differentiation and interpretation of measured phenomena, deeper penetration into the earth's crust, critical geophysical phenomena associated with mineral concentrations, are some of the aspects currently under investigation. Each advance brings more deposits into range of useful exploitation. The need for new discovery presses, for the rate at which minerals are consumed is accelerating, propelled by growing populations, increasing standards of living and industrialization of backward regions. Resources and exploration methods are adequate for now; in the near future lies a problem.

A third factor for consideration is the increasing difficulty of mining as a mineral deposit is worked. At first thought one would assume that experience would improve efficiency and solve the operating problems. But natural conditions offsetting this are unavoidable. Deeper mining and extended workings mean longer distances to transport ore, men and supplies, higher lifts to pump water, and increased supervisory difficulties, all contributing to increased costs per unit produced. In many underground mines depth brings difficulties with support as ground pressure increases, and with higher temperatures which demand an extensive powered ventilation system. Most miners find the grade of ore diminishes with depth and others, mining the best ore first, find that continuance in business requires the mining of lower grade ore. On the whole, these difficulties have been offset by technological improvements in equipment and methods, both in the mine and in the recovery plants. The effectiveness of the engineers in the minerals industry is shown by the prices of the common metals which during the past half-century have been decreasing when priced in constant value dollars, whereas the cost of most other raw materials has been advancing. The mining of lower and lower grade ores extends potential reserves, for such deposits seems to be relatively abundant; the trick is to economically exploit them.

An increasingly important factor in extending metallic resources is the efficiency with which metals are used. The recovery of scrap is a time-honored activity and supplies a large part of the copper, lead, zinc, and steel placed on the market. Many other metals are reclaimed for reuse. Substitute materials have released metals from traditional uses so that the available supply may be used for those purposes having no adequate substitute. Substitution of one metal for another also is a means for conservation, but relative cost is the practical decisive factor in specific cases of replacement. A rapidly growing field involving both conservation and expanded need for unusual metals is the use of alloys. The unique properties of alloys for specific service has on one hand made it possible to design with less material and on the other hand has created a demand for the metals which impart special qualities to the alloys. An enormous field for metallurgical research is open in this general area, for useful application must often be preceded by knowledge of physical properties and occasionally by development of special techniques for compounding or alloying, subsequent fabrication, and heat treatment.

The manufacture of artificial minerals was limited to a few gems until the discovery that carborundum could be produced by the electric furnace and substituted for the

(Continued on page 18)

Mineral Engineering at the University of Washington

1895-1959

Milnor Roberts

Although the Washington State Legislature authorized the establishment of a "School of Mining" in 1893, no formal announcement appeared in the University Calendar until the issue of 1898-1899, when "The College of Mining and Metallurgy" was listed. However, Henry Landes, Professor of Geology, had been giving courses in Mining and Assaying since 1895. In 1900-01 Almon H. Fuller, Dean of the College of Engineering, was listed also as Dean of the "School of Mines." The first degree granted in the College of Engineering was a B.S. in Mining Engineering in 1900.

The following year, Milnor Roberts was appointed Dean of the "College of Mines," a position he held until his retirement in 1947. During his deanship, many useful contributions were made to the mineral industries of the State, and publications dealing with its various mineral resources are still requested. At the Dean's retirement, the chief building devoted to the College's classrooms and laboratories was renamed Milnor Roberts Hall. Dean Emeritus Roberts still takes an interest not only in his former "College" but in many other University activities.

In 1916 the Northwest Experiment Station, one of 12 research laboratories set up by the U.S. Bureau of Mines, was established on the campus. Its staff at present numbers sixteen, with Dr. H. A. Yancey, Chief, Solid Fuels Technology, Region One, U.S.B.M., and Superintendent of Northwest Experiment Station, a post he has held since 1928. Three of the staff members are Lecturers in the School of Mineral Engineering and also cooperate with the faculty in research supervision. The Station is principally concerned with fundamental research in beneficiation of coal and non-metallic minerals and in developing the utilization of Northwest mineral raw materials. Notable among its contributions to mineral technology are the development of the cyclone as a classifying and thickening device, the application of the shaking table to coal cleaning, development of coal preparation by heavy media separation processes, pioneering the techniques and analytical methods for measuring the efficiency and performance of coal-cleaning plants or processes. Over 220 publications have been issued by the Northwest Experiment Station.

Two faculty members who gave long service to the School should be mentioned here. Joseph Daniels, since 1954 Professor Emeritus of Mining and Metallurgical Engineering, originally joined the staff in 1911. His publications, especially those on the coal resources in Washington, are still valid and his services as a consultant in the United States and abroad are in frequent demand.

Hewitt Wilson, who founded the Ceramic Engineering Division in 1920, was notable in his field until his untimely death in 1952. In October, 1955, the Hewitt Wilson Ceramic Laboratory was dedicated.

Drury A. Pifer

Following Dean Roberts' retirement, Drury A. Pifer was appointed Director of the School of Mineral Engineering, which at that time became a division of the College of Engineering.

Professor Pifer, who holds both his B.S. and M.S. degrees from the University of Washington, assumed his post after extensive experience in mining, eight years of which was as manager of mines for DeBeers Consolidated Mines, Ltd., in South Africa. In addition to his administrative duties, he teaches several courses, is active in the mining associations and societies, is a Trustee of the Northwest Mining Association, and engages in consulting practice.

In the fall of 1958, undergraduate registration in the School of Mineral Engineering was 127 (not including freshmen*), and graduate students number 33. With rapidly growing interest in ceramic and metallurgical engineering, the demands on the School's physical facilities are heavy and during the past twelve years there has been almost a complete replacement of laboratory equipment by modern apparatus and instruments. There are eleven men on the teaching faculty.

In addition to curricula in mining, metallurgical and ceramic engineering there are now offered four-year options in geological engineering and in mineral preparation engineering. Graduate studies leading to the degree of Master of Science are offered in the three major fields.

The report of the research activities of the School of Mineral Engineering covers the period October, 1956, to April, 1959. During this period seven M.S. degrees were granted in Ceramic Engineering and Ceramics, six in Metallurgical Engineering and Metallurgy, and three in Mining Engineering.

The wide range of interests pursued in the School is indicated by some of the thesis investigations which included studies of electrical porcelains, the attack of molten iron on refractories, corrosion of plastically deformed stainless steel, methods for measuring the viscosity of mineral slurries, transformations in alloys of copper-tin and copper-beryllium, the formation of mullite, dental porcelains, the performance characteristics of the DSM sieve bend, factors controlling the annealing rate of aluminum, plastic parameters for metals from a new general equation relating stress and strain, and others of like character. Theses are available for consultation in the Engineering Library.

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* Since 1923 the Department of General Engineering has handled all freshman engineering students.

April, 1959

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Clockwise from upper left

Graduate students Mario Gomez and Ed Costello measure metal specimen length changes by recording dilatometer.

Students Dave Siddle, Don Engdahl, and Gary Miller examine mineral products under microscopes.

Professor E. E. Mueller adjusting the fluorescent X-ray spectrograph.

Graduate student Fred Simpson operates the flame-analysis unit of the Beckman spectrophotometer.

Henry Okumura, graduate student, uses the metallograph.

Center: Students Richard Allen and Bob Wolter perform magnetic separation experiment.

Graduate Studies and Research in Mineral Engineering

1956-1959

CERAMIC ENGINEERING DIVISION

EDWARD E. MUELLER
Associate Professor of Ceramic Engineering

PROJECT: Development of a resistive temperature sensing element

SPONSOR: United Control Corporation, Seattle

An evaluation of ceramic coatings with proper electrical insulating characteristics is being made to determine their effiicacies as combined adhesives and potting compounds when used in conjunction with ceramic coated wire as resistive temperature sensors.

PROJECT: Investigation of the effect of paper sludge on structural clay products.

SPONSOR: Simpson Paper Company and Lowell Brick & Tile Company, Everett, Washington

This study is concerned with improving the properties of existing structural products, or the development of new products, through the use of a waste product which is currently being discarded.

PROJECT: Investigation of properties of carbon and graphite

in cooperation with

ROBERT J. CAMPBELL, JR., *Assistant Professor of Ceramic Engineering*

L. N. JOHANSON, *Associate Professor of Chemical Engineering*

SPONSOR: General Electric Company, Hanford, Washington

A determination of various physical property data of carbon and graphite at ordinary and elevated temperatures was made.

JAMES I. MUELLER
Professor of Ceramic Engineering

PROJECT: X-Ray Diffraction Studies of Ceramic Materials

SPONSOR: Engineering Experiment Station

This project, continued over a period of four years, has included investigations into the following areas:

RESEARCH ASSISTANT: M. H. Kamdar

1) The utilization of X-ray diffraction as a means of quantitatively determining the glass content of Al_2O_3 ceramics. These materials, commonly used today as radomes and insulators, require dielectric characteristics within certain fairly narrow limits. This property is materially affected by the presence of crystalline or vitreous impurities. The amount of the former can be ascertained by conventional methods. Results of this work indicate that the analysis of the glass can be accomplished within satisfactory limits by X-ray diffraction techniques. M.S. thesis.

RESEARCH ASSISTANT: Ivene Johnston

2) Precision X-ray diffractometric analysis of the clay mineral, kaolinite, indicated that certain atomic planes of this material produce diffraction lines that have not been previously reported. M.S. thesis.

PROJECT: High-Temperature Diffraction Studies

SPONSOR: Engineering Experiment Station

The prime purpose of this project has been to design, construct, and operate a furnace which can be mounted on an X-ray diffractometer. This would permit investigation of the kinetics of high-temperature reactions.

RESEARCH ASSISTANT: Allen D. Miller

The furnace has been constructed and is under test at present. M.S. thesis.

RESEARCH ASSISTANT: Lavada A. Moudy

An investigation is being made of the kinetics of oxidation at elevated temperatures in the uranium-oxygen system.

PROJECT: Molten Iron Attack on Refractories

SPONSOR: Gladding, McBean & Company

Earlier work on this project consisted of developing a satisfactory test method for this study. This has been completed and initial tests have been performed to ascertain the resistance of various refractory materials to attack by pure molten iron. Since its inception, it has covered three fellowships, with two M.S. theses completed and one nearly completed.

PROJECT: The Mechanics of Stiff-Mud Extrusion

SPONSOR: The Edward Orton, Jr., Memorial Foundation

This project has been continuing for a period of five years. Its purpose has been to study the flow of clay through extrusion barrel and die in stiff-mud extrusion. A method has been devised utilizing strain gages to measure the force applied to the die face and to relate this force to the rate of flow through various types of orifices. Three M.S. theses.

PROJECT: X-Ray Studies of Highly Radioactive Materials

SPONSOR: Pratt & Whitney Aircraft Company

The object of this work was to modify existing commercial X-ray diffraction and fluorescent spectrographic equipment to permit the study of irradiated materials whose radioactivity was in the range of 5 to 5 R/hr (at 17 cm). This phase has been completed and current investigations are proceeding on the character of the samples.

METALLURGICAL ENGINEERING DIVISION

RICHARD H. LLOYD

Assistant Professor of Metallurgical Engineering

PROJECT: Rhodium Plating Investigation

SPONSOR: Boeing Airplane Company

An investigation was carried out to determine the cause for excessive rejects of rhodium plated parts. Manufacturing and inspection techniques were studied and these correlated with the actual in-use requirements of the parts.

PROJECT: X-Ray Spectroscopic Analysis for Cu in Lead Bullion and PbO-SiO_2 Slag

A rapid method of analyzing for copper in lead metal and slag was needed in conjunction with one of the student experiments. This project developed an X-ray spectroscopic analysis which made use of an external standard. A satisfactory method was developed and several features of external standards were revealed and investigated. (M.S. thesis)

PROJECT: Sulfation of Manganese Ores

This is an investigation of the sulfation kinetics of manganese oxides, manganese silicates, and the natural oxide and silicate ores of manganese. The investigation centers around the gas-solids reaction where SO_3 or SO_2 and O_2 are reacted with the solids to form $MnSO_4$, which is water soluble. This allows the extraction of manganese from low grade ores by hydrometallurgical techniques.

DOUGLAS H. POLONIS

Associate Professor of Metallurgical Engineering

PROJECT: Studies of Tantalum Alloys and Columbium Metal

SPONSOR: Electro Metallurgical Company

One aspect of this work was concerned with the constitution of several tantalum base alloys resulting from various heat treatments. The work on columbium included separation and identification of minor impurity phases and the effects of minor impurities on deformability. Phase identifications were accomplished by metallographic and X-ray methods.

PROJECT: Titanium Alloy Studies

SPONSOR: Electro Metallurgical Company

This project involved studies of the precipitation of Ti_2Cu from supersaturated alpha solid solutions in the Ti-Cu system. The precipitation reaction was followed by means of electrical resistance and microhardness measurements. Additional studies were conducted on the constitution of titanium-rich alloys of titanium and lead. Preliminary work on the latter project involved experimentation with hot-stage metallography and high-temperature X-ray methods.

PROJECT: A Study of the Beta Phase Decomposition in a Eutectoid Copper-Beryllium Alloy

SPONSOR: Engineering Experiment Station

RESEARCH ASSISTANT: Donald M. Montgomery

This project was concerned with the decomposition of β phase during heat treatment at temperatures below the eutectoid temperature. X-ray diffraction studies revealed the formation of two transitional phases during quenching from the β-phase field to room temperature. The decomposition reaction $\beta \rightarrow \alpha + k$ was studied by means of the X-ray diffractometer and metallographic methods. M.S. thesis.

PROJECT: Transformation Studies of the Delta and Gamma Eutectoid Alloys of the Cu-Sn System

GRADUATE STUDENT: Ronald D. Nelson

Studies were conducted on the isothermal decomposition of δ phase in powder specimens of a 32.6 wt% Sn alloy. The project also involved X-ray and metallographic studies of the quenched γ phase alloy (27.1 wt% Sn) and the isothermal decomposition of γ phase at several temperatures. M.S. thesis.

PROJECT: The Effect of Aluminum on the Recrystallization of Alpha Titanium

SPONSOR: Engineering Experiment Station

RESEARCH ASSISTANT: Robert A. Woodall

The effect of low aluminum contents (less than 4 wt%) on the rate of recrystallization of α Ti is being investigated. The associated microstructural changes and the effects of varying degrees of cold work on recrystallization and subsequent grain growth are included in this study.

PROJECT: A Study of the Decomposition of the Alpha Prime Phase of the System Titanium-Copper

SPONSOR: Engineering Experiment Station

RESEARCH ASSISTANT: Mario Pio Gomez

This research involved a study of the kinetics of decomposition of the alpha prime phase in a Ti-Cu eutectoid alloy. In addition, the equilibrium constitutions of alloys containing 25 atomic % Cu and 33.3 atomic % Cu were investigated in order to clarify the discrepancy regarding the possible existence of an intermetallic phase Ti_3Cu. Quantitative reaction rate data have been obtained which indicate that the decomposition of alpha prime is accurately described by a log autocatalytic type of rate equation. M.S. thesis.

PROJECT: Phase Transformation Studies in Copper-Silicon Alloys

SPONSOR: Engineering Experiment Station

RESEARCH ASSISTANT: Gary Dreyer

This research involves a study of the effects of quenching and aging on the constitution of Cu-Si alloys containing 4.9% Si. The decomposition of supersaturated α phase is being studied by means of metallography, electrical resistance, and X-ray diffraction techniques. The project is intended to develop a detailed understanding of the structural changes occurring during the precipitation of γ phase from α phase.

EARL C. ROBERTS
Professor of Metallurgical Engineering

PROJECT: Tin Whisker Studies
SPONSOR: Boeing Airplane Company

This project involved an investigation of the growth of tin whiskers on copper and steel sheet. One of the objectives was to see if the whisker root area could be observed by high magnification metallography. A second portion of the problem was to observe the relation between tin plate thickness and the elastic strain in the tin lattice. This latter involved an X-ray spectroscopy and X-ray diffraction study of samples plated to known thicknesses.

PROJECT: Oxidation Studies of Titanium-6 Aluminum-4 Vanadium Alloy
SPONSOR: Boeing Airplane Company

The object of this investigation was to determine the relationship between the oxygen concentrations in the surface of the above alloy sheet and the formability of the metal.

PROJECT: High Temperature Bearings
SPONSOR: Boeing Airplane Company

Bearings capable of supporting a load of 10,000 psi for one-half hour at 1800° F were required, with specific limitations as to oxidation, coefficient of friction, and amount of wear. A series of oxidation-resistant coatings of high hardness were applied by various means to molybdenum sheet of commercial purity to satisfy the above requirements.

PROJECT: Metal Forming Parameters
SPONSOR: Boeing Airplane Company
RESEARCH ASSISTANT: Donald L. Paulson

This project developed a method whereby plastic forming parameters for metals of widely differing physical characteristics might be determined from true stress-true strain data. M.S. thesis.

PROJECT: Annealing of Polycrystalline Aluminum
GRADUATE STUDENT: William E. Anderson

The object of this work was to study rate-controlling factors in the annealing of compressionally deformed aluminum specimens of different degrees of purity. M.S. thesis.

PROJECT: Rate of Solution of Graphite in Ductile Iron
GRADUATE STUDENT: M. H. Kamdar

This work was a kinetic study aimed at determining rate of solution of nodular graphite in ductile iron. X-ray diffraction, metallography, and hardness testing were used to follow the course of the reaction.

PROJECT: Effects of Thermal Expansion on a Uniaxially Confined Cylinder of 5052-H34 Alloy
GRADUATE STUDENT: Richard E. Holt

This project showed the difference in annealing behavior resulting from heating a cold-worked cylindrical specimen of an aluminum alloy under conditions of free expansion or while under conditions of physical restraint. M.S. thesis.

PROJECT: Plastic Deformation and Annealing Studies of Ductile Iron
SPONSOR: Engineering Experiment Station
RESEARCH ASSISTANT: Curtis D. Brownfield

This work was done to analyze the recrystallization behavior of cold-worked ductile iron. Recrystallization curves and tensile test data were obtained and the effect of deformation and temperature on the grain size were recorded. M.S. thesis.

MINING ENGINEERING DIVISION

DONALD L. ANDERSON
Associate Professor of Mining Engineering

PROJECT: Examination and evaluation of iron ore deposits on the Pacific Coast of the State of Baja California, Mexico

The evaluation of this hematite-magnetite iron ore was undertaken for and the report submitted to a Seattle syndicate interested in the development of these deposits.

PROPECT: Evaluation of a gold placer deposit on the Pacific Coast of Costa Rica

This project was undertaken for a Seattle group interested in this development. Report submitted.

PROJECT: Examination and appraisal of a placer mine in the Peshastin Creek District, Chelan Co., Washington, in conjunction with highway construction in the Blewett Pass area
SPONSOR: State of Washington

This assignment was completed for and the report submitted to the Attorney General's Office in cooperation with the State Department of Highways.

FREDERICK B. BRIEN
Associate Professor of Mineral Engineering

PROJECT: Flotation of Chromite from Olivine
GRADUATE STUDENT: Evan A. Lowe

A chromite ore from the State of Washington, which had previously resisted concentration by means of flotation, was investigated. Numerous variables were examined and a selective flotation procedure was developed. The study was then aimed at explaining the fundamental mechanisms of the separation in order to gain information that might prove useful in other flotation problems. M.S. thesis.

PROJECT: An Investigation of the Use of Deep Bubble Columns in Flotation in Difficult Mineral Separations
GRADUATE STUDENT: Donald Hood

It is recognized that in mineral flotation some degree of selection is obtained by bubble sorting action in the froth column. An investigation is being

(Continued on page 32)

THE FLOTATION OF CHROMITE FROM OLIVINE

FREDERICK B. BRIEN
Associate Professor of Mineral Engineering

EVAN A. LOWE
Graduate Student in Mineral Engineering

F. B. Brien

The purpose of this project was to investigate the use of flotation for the concentration of chromite from olivine. Upon attaining a satisfactory degree of selectivity, the investigation comprised testing of variables for optimum conditions and assessing flotation mechanisms.

The project presented technological interest in that conventional chromite flotation procedures have been rather difficult to reproduce. Commercial application has been insignificant, principally because of low recoveries, the necessity for using slime-free pulps, and the need for extensive cleaning and recleaning circuits. The project has also a local economic aspect in relation to the extensive deposit of chromite-bearing olivine located in the Twin Sisters Mountain area of Northwestern Washington, ore from which has previously resisted concentration by means of flotation. The ore from the Twin Sisters deposit used in this investigation was taken from the Begonia claim. (See Figs. 1 and 2.)

A microscopic examination of the ore samples indicated that the chromite occurred in grains varying in size from 0.1 to 1.25 mm (Fig. 3), with a predominance in the 0.5- to 0.6-mm range. The matrix was essentially olivine, relatively free from alteration; several scattered occurrences of unaltered enstatite also were noted, representing a small percentage of the silicates. There was some occurrence of fine olivine crystals disseminated within the coarser chromite grains, averaging 0.1 mm in size. The head assays on the two samples used in testing ran 25.4 and 24.7 per cent Cr_2O_3.

The principal minerals were separated into clean fractions by means of the Franz isodynamic separator and heavy liquids. The chemical analyses for each are contained in Table I.

The analysis indicates that the deviation from the ideal 68 per cent Cr_2O_3 of theoretical chromite ($FeO\ Cr_2O_3$) is due to isomorphous substitution of magnesium for ferrous iron and aluminum for trivalent chromite.

The chromite did not react to common solvents; however, the olivine was relatively reactive, as indicated in Table II.

E. A. Lowe

Preliminary flotation tests were carried out using conventional procedures, but selectivity was not achieved. The first selectivity was obtained by using a procedure under development on other chromite ores by the U.S. Bureau of Mines, Mineral Dressing Section, Albany, Oregon. This procedure was as follows:

1) Dry or wet grinding, pulping to notation density, addition 2 lb sodium fluoride and 10 lb No. 2 fuel oil per ton of solids. Condition 5 minutes.
2) Addition of 10 lb of emulsion per ton of solids. The emulsion was made up of "liqro" tall oil and "Petroflote 130" petroleum sulfonate in water, weight ratio 9 : 1 : 90, respectively. Condition 3 minutes.
3) Addition of 4 lb sulfuric acid per ton of solids. Condition 2 minutes.
4) Rougher float followed by three stages of cleaning, with two additions of 2 lb sulfuric acid per ton of solids in each cleaning stage.

Modifications to the above procedure were made in obtaining optimum selectivity with the Twin Sisters sample. The "liqro" tall oil was replaced with reagent grade oleic acid, the No. 2 oil, by domestic stove oil. The use of "Petroflote" petroleum sulfonate was discontinued, as was the emulsification procedure. The ore was wet ground, the fatty acid, fuel oil, and sodium fluoride were added in the grinding stage. The addition of acid was made

TABLE I
ANALYSIS OF OLIVINE AND CHROMITE

Mineral	%	%
Cr_2O_3	.....	50.0
MgO	50.5	14.9
Al_2O_3	2.28	18.2
SiO_2	41.8	.....
FeO	3.98	0.56
Fe_2O_3	4.95	19.8
Total Fe	6.10	14.3
Cr-to-Fe ratio	.....	2.4-to-1

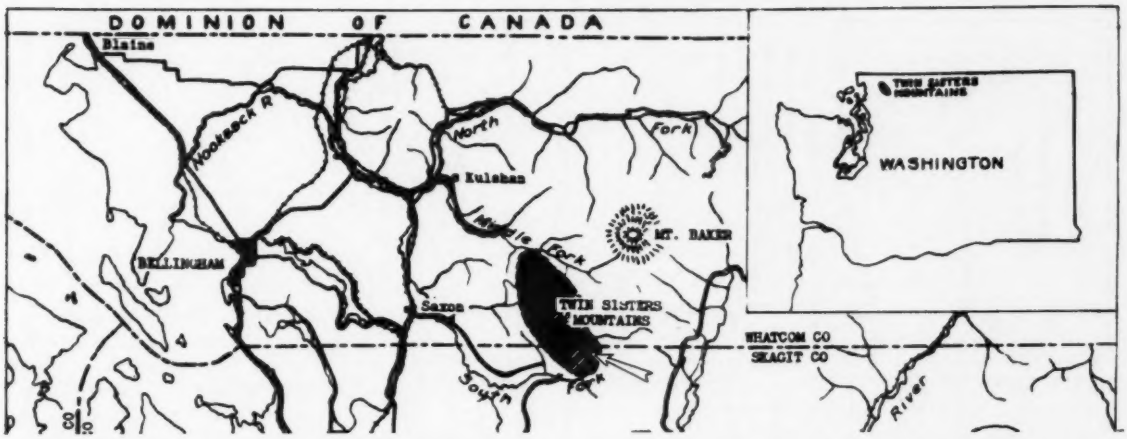

FIG. 1. INDEX MAP OF NORTHWESTERN WASHINGTON SHOWING THE LOCATION OF THE BEGONIA CLAIM

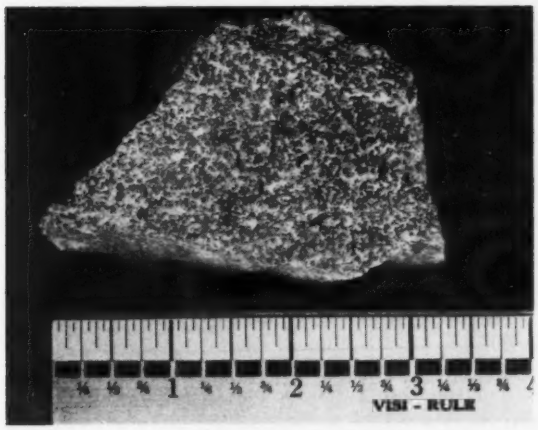

FIG. 2. HAND SPECIMEN OF THE BEGONIA CHROMITE

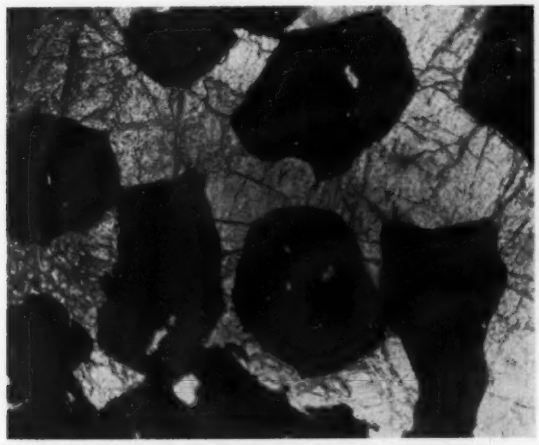

FIG. 3. MICROSCOPIC FEATURES OF THE BEGONIA CHROMITE

FIG. 4. ARRANGEMENT OF LABORATORY FLOTATION EQUIPMENT

Note pH electrodes immersed in pulp. Burette to the right allows continuous addition of acid, thus insuring very close pH control.

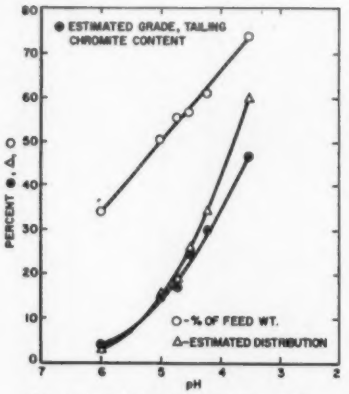

Fig. 5. Variation in Rougher Tailing with pH

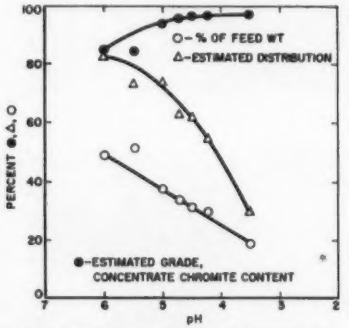

Fig. 6. Variation in Cleaner Concentrate with pH

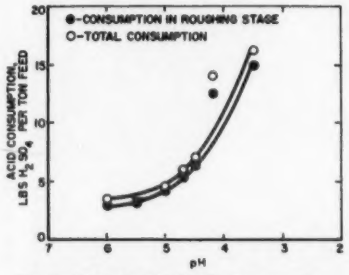

Fig. 7. Variation in H_2SO_4 Consumption with pH

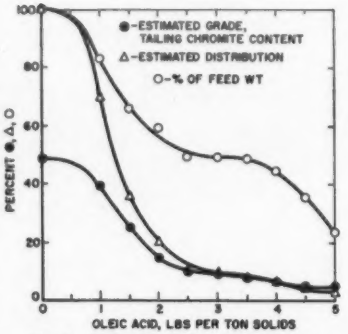
●-ESTIMATED GRADE, TAILING CHROMITE CONTENT
Δ-ESTIMATED DISTRIBUTION
O-% OF FEED WT
PERCENT ●, Δ, O
OLEIC ACID, LBS PER TON SOLIDS

Fig. 8. Variation in Rougher Tailing with Oleic Acid Dosage

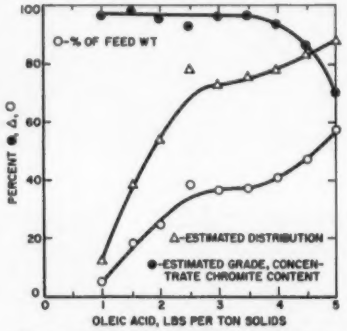
O-% OF FEED WT
Δ-ESTIMATED DISTRIBUTION
●-ESTIMATED GRADE, CONCENTRATE CHROMITE CONTENT
PERCENT ●, Δ, O
OLEIC ACID, LBS PER TON SOLIDS

Fig. 9. Variation in Cleaner Concentrate with Oleic Acid Dosage

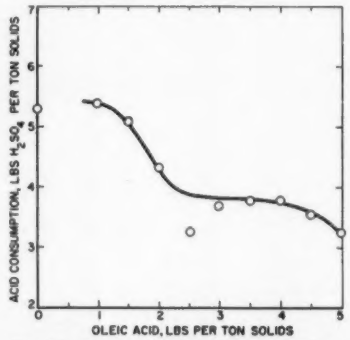

Fig. 10. Variation in H_2SO_4 Consumption with Oleic Acid Dosage

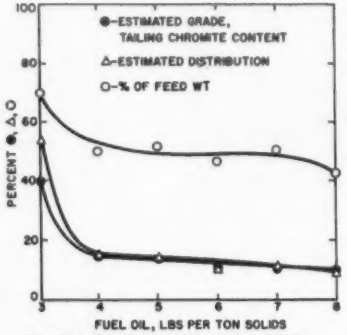

Fig. 11. Variation in Rougher Tailing with Fuel Oil Dosage

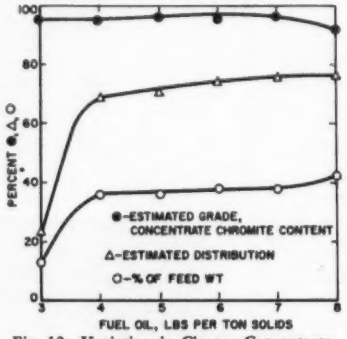
●-ESTIMATED GRADE, CONCENTRATE CHROMITE CONTENT
Δ-ESTIMATED DISTRIBUTION
O-% OF FEED WT
PERCENT ●, Δ, O
FUEL OIL, LBS PER TON SOLIDS

Fig. 12. Variation in Cleaner Concentrate with Fuel Oil Dosage

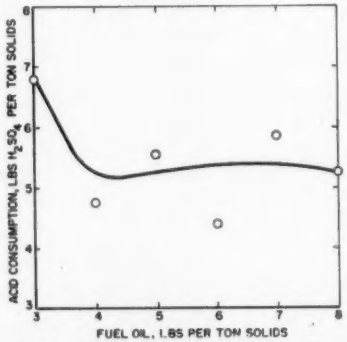

Fig. 13. Variation in H_2SO_4 Consumption with Fuel Oil Dosage

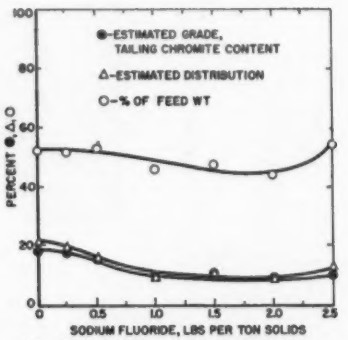
●-ESTIMATED GRADE, TAILING CHROMITE CONTENT
Δ-ESTIMATED DISTRIBUTION
O-% OF FEED WT
PERCENT ●, Δ, O
SODIUM FLUORIDE, LBS PER TON SOLIDS

Fig. 14. Variation in Rougher Tailing with Sodium Fluoride Dosage

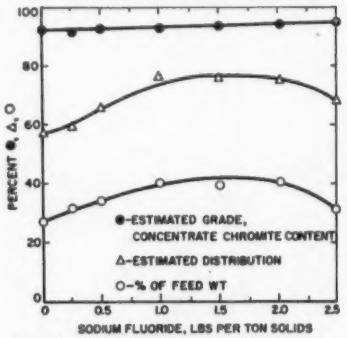
●-ESTIMATED GRADE, CONCENTRATE CHROMITE CONTENT
Δ-ESTIMATED DISTRIBUTION
O-% OF FEED WT
PERCENT ●, Δ, O
SODIUM FLUORIDE, LBS PER TON SOLIDS

Fig. 15. Variation in Cleaner Concentrate with Sodium Fluoride Dosage

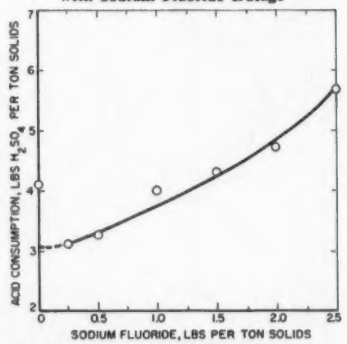

Fig. 16. Variation in H_2SO_4 Consumption with Sodium Fluoride Dosage

TABLE II

SOLUBILITY OF OLIVINE

Size (mesh)	Sample Wt (g)	Leaching Conditions			Ions in Solutions (g/l)	
		Solvent	Vol. (ml)	Contact time	Mg^{++}	Fe^{++}
−100+150	20.0	H_2SO_4, pH3	200	2.0 hr	0.41	0.11
−100+150	20.0	Distilled water	200	10 days	0.24	....

continuously to the flotation cell, a Fagergren type, while pH electrodes immersed in the flotation pulp allowed continuous monitoring of the acidity (Fig. 4). One cleaning step was used, sulfuric acid being added at this point as required to maintain the desired pH.

Upon achieving a satisfactory degree of selectivity, tests were planned in order to determine the effects of variables, establish optimum conditions, and investigate the mechanisms involved. Variables tested were (a) pH over the range 3.5 to 6.0, in both the rougher and cleaner stages (Figs. 5,6,7), (b) oleic acid addition up to 5.0 lb per ton of solids (Figs. 8, 9, 10), (c) fuel oil addition from 3.0 to 8.0 lb per ton (Figs. 11,12,13) and the effect of adding some portions of the fuel oil to the flotation cell rather than to the grinding circuit, (d) sodium fluoride addition from zero to 2.5 lb per ton of solids (Figs. 14, 15, 16), (e) fineness of grind.

Owing to the ease with which the chromite could be distinguished visually from the olivine, a microscopic examination allowed assessment of the flotation products, and chemical analysis checks indicated that the results were well within the accuracy required for indicating the effects of variables. The use of this analytical procedure expedited the test work to a considerable degree. Since investigation of the fluoride mechanism required the use of an analytical method for fluoride ion, a colorimetric method was used.

Two essential flotation steps were necessary for separating the chromite from the olivine. In the first step, the minerals were subjected to the conditioning action of sodium fluoride and to the collecting action of the two organic reagents, oleic acid and fuel oil. In the second step, sulfuric acid was added to the collected pulp, whereupon an immediate selectivity took place and the chromite was floated readily from the olivine. The separation was rapid, indicated high selectivity and recovery, and took place in the presence of slimes.

The experimental results indicated that in the first flotation step all particles were collector-coated, in the second, the olivine was differentially depressed. The mechanisms of collection were indicated by the early tests, which showed that, while no collection was obtained by use of fuel oil alone and only weak collection by oleic acid alone, all particles adhered tenaciously to air bubbles when combinations of both reagents were employed. It was evident that the strong collection was due to the spread of a reinforcing film of neutral oil over surfaces already weakly collected with fatty acid molecules.

The explanations of the mechanisms of collection offered by Taggart and Arbiter[6] agree quite well with the results noted in this part of the investigation. It is believed that the collection of chromite particles was accomplished by formation of a chromium oleate surface layer surrounded by a reinforcing film of neutral oil. According to Schulman and Smith,[3] chromium hydroxide forms at a pH of 5.28. As determined by the experimental studies, the optimal pH of the roughing operation fell near 5.1. The depression of chromite occurring in pulps of higher acidity was thus due to rupture of the chromium oleate bonds at the particle surfaces, with reversion of the oleate to the acid molecule state.

The initial collection of olivine was likewise believed due to the formation of a neutral magnesium and iron soap layer enveloped by fuel oil. The depression of olivine, however, did not come about wholly by reversion of the oleates to the acid form. Results indicated that depression of olivine was primarily caused by dissolution of the particle surfaces. It was shown in the preliminary study of the minerals that the olivine surfaces were prone to release iron and magnesium cations in dilute acid and even in distilled water solutions. The rate of dissolution was not rapid but sufficient to maintain the olivine surfaces too mobile to support stable collector coatings.

A secondary contribution was imparted by fuel oil in the froth phase. The effect of the fuel oil was to prevent formation of a stable persistent froth, and thus to prevent entrainment of slime gangue between persistent bubble walls. Observation suggested that the oleic acid was prevented by the oil from manifesting its polar properties to cause normal reduction in surface tension at water-air interfaces, thus reducing frothing characteristics. In the flotation tests near the end of the froth removal stage, an inversion to a persistent elastic froth occurred. The cause

TABLE III

METALLURGICAL RESULTS FOR THE FINAL TESTS*

Product	Weight		Assays (%)		Unit Content Cr_2O_3	Distribution Cr_2O_3 (%)	Ratio Cr:Fe
	(g)	(%)	Cr_2O_3	Fe			
Cleaner concentrate	297	48.4	47.41	13.98	22.93	93.0	2.32
Cleaner tailing	44	7.2	11.74	7.04	0.84	3.40	
Rougher tailing	273	44.4	2.02	10.12	0.90	3.60	
		100.0				100.0	
Calculated head	614				24.67		

Regrant consumption

Oleic acid	2.8 lb/ton
Fuel oil	6.5 lb/ton
Sodium fluoride	2.0 lb/ton
Sulfuric acid	2.7 lb/ton

pH conditions

Seattle city tap water	7.5
Ground pulp after dilution	8.9
Rougher stage	5.2
Cleaner stage	4.9

* All chemical analyses were made by Technical Services Laboratory, U.S. Bureau of Mines, Albany, Oregon.

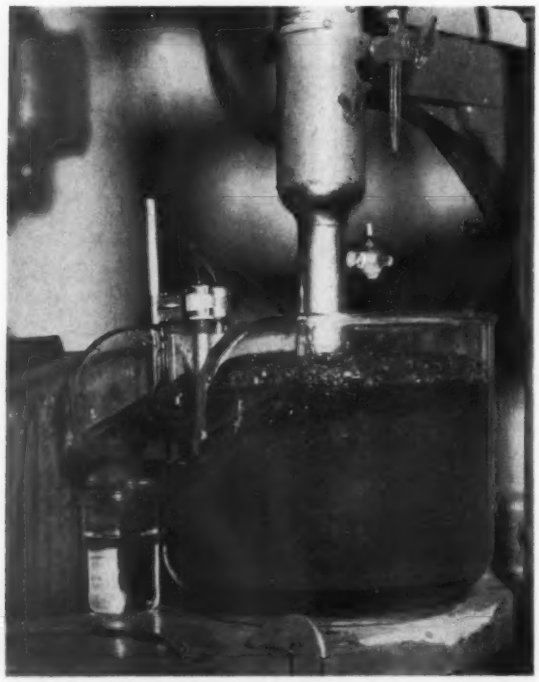

FIG. 17. SEPARATION OF CHROMITE IN THE ROUGHING STAGE

of this transition was quite apparent from a consideration of the distribution patterns of the fatty acid and neutral oil. During flotation both the fuel oil and the fatty acid left the cell as collector coatings on particle surfaces; however, the hydrophobic character of the neutral oil dictated that it be concentrated in the air phase at a faster rate. The pulp therefore became depleted in fuel oil and the oleic acid was permitted to exercise its surface tension characteristics, whereupon the froth color gradually changed to a dull brown from entrainment of slime olivine. A supplementary addition of fuel oil retarded this phenomenon. In the cleaner operations the tendency for transition to a persistent elastic froth was barely discernible, reflecting the accumulation of fuel oil in the rougher froth as well as the effect of a supplementary addition of oil.

The effects of sodium fluoride were comparably as significant as those of fuel oil in the tests. Increasing fluoride concentration caused a small continuous increase in grade of concentrate mainly due to rejection of slime olivine. In the absence of fluoride, the chromite was weakly collected, and the froth slimy and persistent. Analytical results indicated that the fluoride concentration was reduced by 25 per cent in pulp water during grinding.

The experimental evidence indicated that there was extensive removal of iron and magnesium ions by formation of insoluble fluorides[5] in preference to the formation of iron and magnesium oleates or hydroxides. The possibility that the depletion of fluoride during grinding may have been due to the participation of hydrofluoric acid was ruled out by the alkaline environment (pH 9). If the formation of hydroxides had occurred, the subsequent acidification step in the flotation cell would have released free

(Continued on page 32)

SPECIAL RESEARCH EQUIPMENT IN PHYSICAL METALLURGY

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E. C. Roberts

The continually increasing need for more quantitative data on the behavior of metals under different conditions of physical environment has created a parallel requirement for highly specialized equipment by means of which the necessary information can be obtained. It is the purpose of this paper to discuss a number of such items of special equipment which have been constructed and are in current use in the Metallurgical Laboratories at the University of Washington. In the main, the instruments are especially adapted to the investigation of solid-state changes in metals which occur at different rates for different conditions of physical circumstance or with changes in chemical composition. Frequently more than one instrument must be used in order to observe the influence of the treatment on more than one physical property and thus provide a more complete analysis of the reaction. It should be pointed out that standard metallurgical equipment still retains much of its inherent value in this work, and specialized devices simply enable a more detailed analysis of the information to be obtained through conventional investigations.

Electrical Resistance Apparatus

This equipment is of great importance in following the kinetics of solid-state reactions because the conductivity of alloys is frequently very sensitive to the amounts of solute components in solid solution. A precipitation reaction in which a metastable single phase transforms to a more stable state, by the precipitation of one or more new phases, is a typical example of a reaction in which the electrical resistance of the alloy can be expected to show an overall decrease, and this equipment allows such changes that occur to be accurately followed.

The apparatus involves a somewhat specialized Double Kelvin Bridge circuit that is particularly useful for measuring resistivity changes in high conductivity materials. Small specimens about one-quarter inch in diameter and three inches long can be employed, and if greater accuracy is desired they can be immersed in liquid nitrogen to lower the thermal component of resistance. This instrument was constructed through the assistance of the Engineering Experiment Station. The circuit diagram and a list of recommended components were generously furnished by W. F. Flanagan and P. A. Flinn.* Figure 1 shows a specimen-holding device designed by one of the authors. Figure 2 shows a composite curve plotted to illustrate the kinetics of tempering in three low alloy steels. Three different reactions are shown here in each steel. They can be separated by the changes in resistivity as a function of time.

D. H. Polonis

Magnetic Balance

Stainless steels which are completely or largely nonferromagnetic are a highly important group of alloys in many structural applications. A ferromagnetic phase can be formed in these alloys either by deformation at low temperatures, or by simple exposure to low temperatures. The alloy 17-7 PH is an example of an alloy of the second type, e.g., it is primarily nonferromagnetic and is subject to transformation at low temperatures. The amount of transformation is a function of time of low-temperature exposure, and consequently the kinetics can be followed by magnetic means.

The magnetic balance arrangement includes a simple electromagnet made up of a soft iron core about which a number of turns of plastic-coated copper magnet wire has been wound. This electromagnet is suspended over the left balance pan of a standard Chainomatic balance. If a small sheet specimen is transformed by subzero quenching, the amount of magnetic phase can be determined by first weighing the specimen normally and then with current flowing through the electromagnet. The difference in

* Formerly graduate students in the Department of Metallurgy at M.I.T.

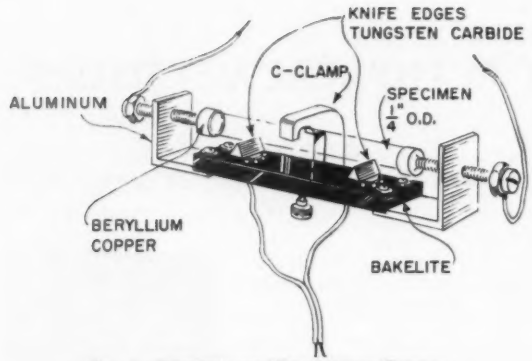

FIG. 1. RESISTANCE MEASURING DEVICE

weight obtained from these two measurements can then be converted to a percent change in weight which is directly proportional to the increase in amount of magnetic phase.

Each specimen is located at a fixed distance from the face of the electromagnet, and check measurements on sheet specimens can be made by inverting so that opposite faces of the specimen are exposed to the surface of the magnet. Figure 3 shows the results obtained by magnetic measurements on 17-7 PH stainless steel samples following subzero quenching to –100° F for different time intervals and a plot of the changes in electrical resistance following an identical treatment.

Gas Quenching Furnaces

The heat treatment of reactive metals requires vacua or inert gas atmospheres if severe oxidation is to be avoided at temperatures in the vicinity of 1000° C. If it is necessary to quench specimens directly from elevated temperatures, specimen removal from an enclosed furnace system becomes a major problem. Quenching liquids cannot normally be incorporated in an enclosed furnace since their vapors may lead to undesirable surface reaction with the metal specimens (oxidation). Quenching in an external liquid can involve delay which may lead to undesirable reaction in a specimen because of partial cooling prior to quenching. Furthermore, water quenching of reactive metal specimens invariably results in surface oxidation which may be undesirable in powder specimens or small samples which are to be used in X-ray studies.

In quenching titanium and zirconium alloys, it is important to make sure that there is no possibility of contamination. These metals and their alloys exhibit solid solubility for oxygen, and relatively minor amounts of this contaminant may appreciably alter the equilibrium constitution typical of an oxygen-free material.

Two special quenching furnaces have been constructed in recent research projects to minimize the

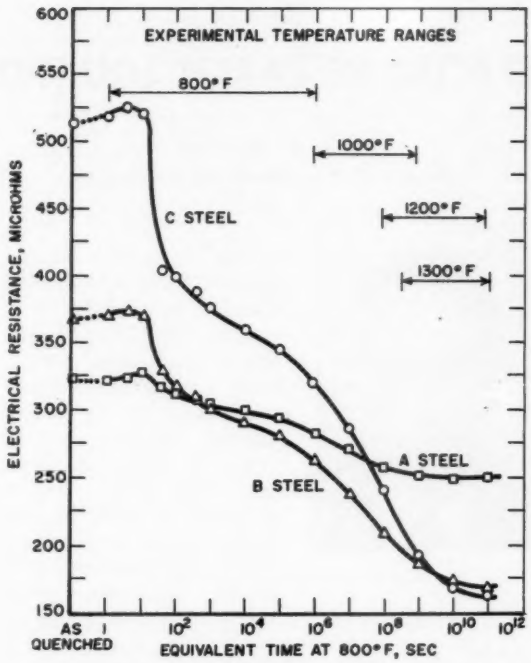

FIG. 2. CHANGES IN ELECTRICAL RESISTANCE OF 4.5% CHROMIUM STEELS ON TEMPERING AT VARIOUS TEMPERATURE RANGES (All referred to equivalent times)

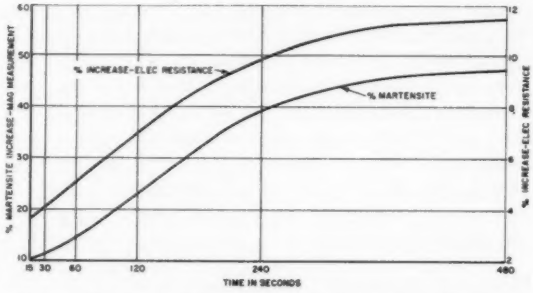

FIG. 3. PERCENT MARTENSITE INCREASE AND PERCENT ELECTRICAL RESISTANCE INCREASE AT –100° F (Times: from 15 through 480 seconds)

contamination problem and delays in quenching time. Both of these furnaces were designed for inert gas quenching. Specimens are heated very rapidly to elevated temperatures and can be quenched directly to room temperature by a jet of helium or argon. Since specimens are quenched directly from furnace temperatures, the problem of delay is also solved.

Lump Quenching Furnace. Figure 4 shows a gas quenching furnace for heating and quenching small (approximately $\frac{1}{8} \times \frac{1}{8} \times \frac{1}{16}$) lump specimens. The design is a simplified version of the type used by Greninger for Ms temperature determinations in

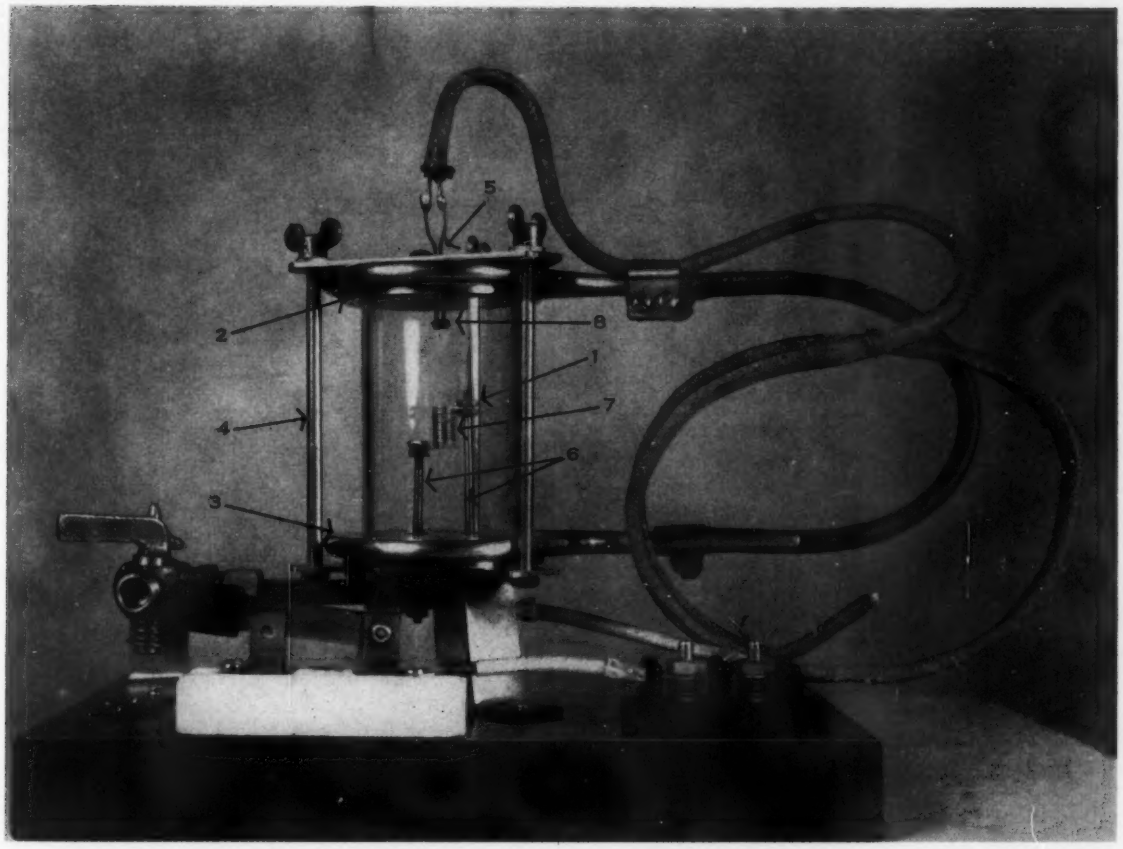

FIG. 4. GAS QUENCHING FURNACE FOR SMALL LUMP SPECIMENS

steels.[1] The main components (see Fig. 4) are as follows:

1. Vycor tubing 1-$^{23}/_{32}$ in. ID, 3 in. long, with ends ground flat
2, 3. Top and bottom copper plates which are in contact with water-cooled copper tubing as shown. These are grooved for neoprene O-ring gaskets which provide an airtight fit with the vycor cylinder.
4. Assembly bolts
5. Kovar thermocouple terminal
6. Power leads
7. Platinum-rhodium or molybdenum resistance heating element (24-gage wire)
8. Terminals for attaching Pt–Pt+10% Rh thermocouple wire

The auxiliary supply system for the quenching gas includes a gas accumulator tank which is pressurized slightly above atmospheric pressure from a cylinder of argon or helium. The accumulator tank is brought to pressure before each run and serves as a gas reservoir for quenching the specimens in the furnace. It is connected to a three-way valve which is in turn connected to the bottom of the furnace and to the vacuum pump. The three-way valve enables evacuation of either the furnace or the gas supply system independently. All connections are made with copper tubing and the joints are sealed with soft solder to ensure freedom from leaks. The system has been capable of a vacuum of 0.1 micron pressure (10^{-4} mm Hg).

The metal specimens for heat treatment are attached to the end of the thermocouple and suspended inside the heating coil. The system is then enclosed and evacuated, and current is applied to the coil through an autotransformer. It has been possible to heat small specimens from room temperature to 1000° C in approximately two minutes without overloading the resistance coil. This temperature can be maintained for an indefinite time, and quenching can be performed by simultaneously cutting the power and introducing gas into the furnace chamber from the accumulator tank. The specimen is quenched by

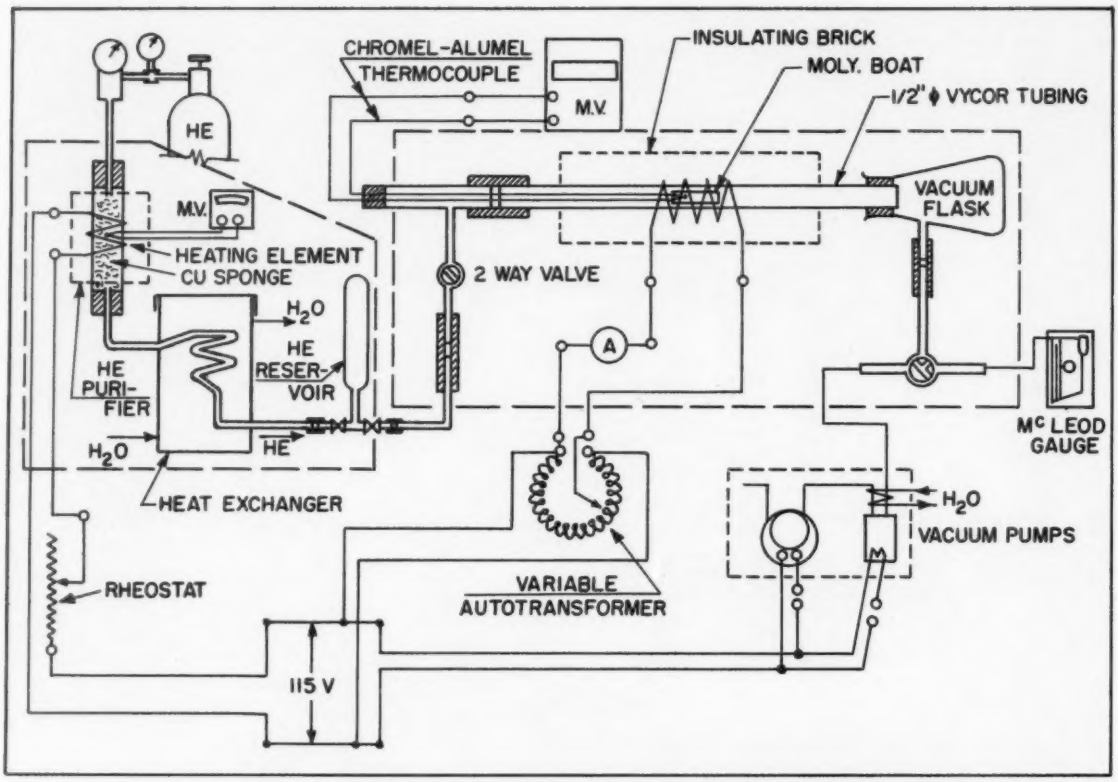

FIG. 5. GAS QUENCHING FURNACE FOR POWDER SPECIMENS AND ACCESSORIES

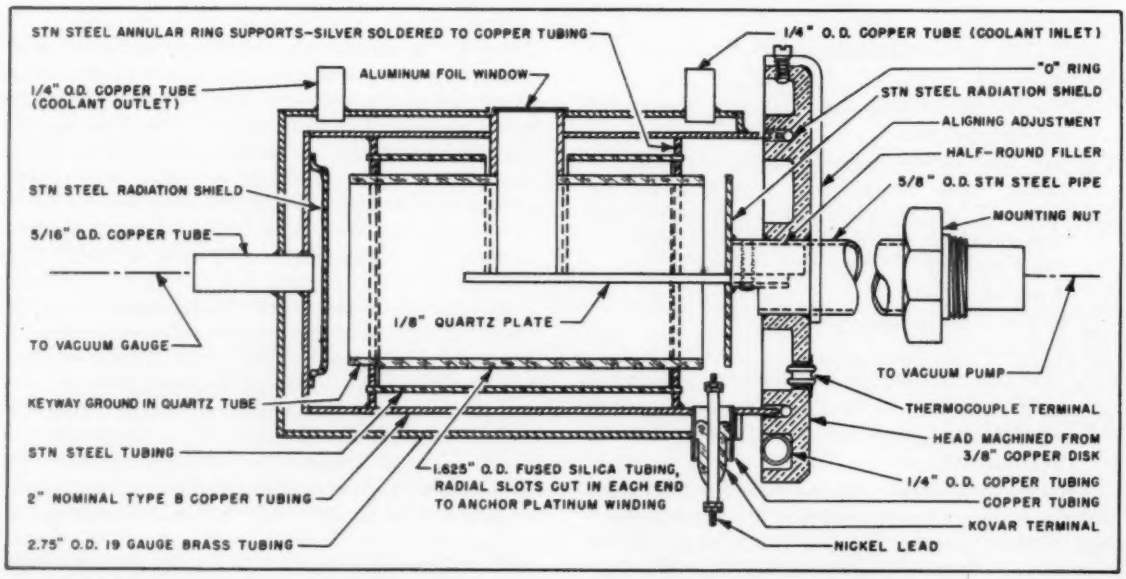
STN STEEL ANNULAR RING SUPPORTS–SILVER SOLDERED TO COPPER TUBING
1/4" O.D. COPPER TUBE (COOLANT INLET)
ALUMINUM FOIL WINDOW
1/4" O.D. COPPER TUBE (COOLANT OUTLET)
"O" RING
STN STEEL RADIATION SHIELD
ALIGNING ADJUSTMENT
HALF–ROUND FILLER
5/8" O.D. STN STEEL PIPE
STN STEEL RADIATION SHIELD
MOUNTING NUT
5/16" O.D. COPPER TUBE
1/8" QUARTZ PLATE
TO VACUUM GAUGE
TO VACUUM PUMP
KEYWAY GROUND IN QUARTZ TUBE
THERMOCOUPLE TERMINAL
STN STEEL TUBING
HEAD MACHINED FROM 3/8" COPPER DISK
1.625" O.D. FUSED SILICA TUBING, RADIAL SLOTS CUT IN EACH END TO ANCHOR PLATINUM WINDING
1/4" O.D. COPPER TUBING
2" NOMINAL TYPE B COPPER TUBING
COPPER TUBING
KOVAR TERMINAL
2.75" O.D. 19 GAUGE BRASS TUBING
NICKEL LEAD

FIG. 6. SCHEMATIC DRAWING OF HIGH-TEMPERATURE ATTACHMENT FOR THE NORELCO X-RAY DIFFRACTOMETER

a brief blast of gas directed through the inlet in the base plate. The estimated quenching rate is in excess of 1000° C per second for the very small specimens.

Platinum heating coils perform well and will endure for many heat treatments. Molybdenum coils should be replaced every three or four runs but are easy to prepare and are much cheaper. This unit has performed well in rapid quenching of titanium alloy specimens.

Powder Quenching Furnace. A second type of gas quenching furnace has been designed specifically for heat treatment of metal powders which can be conveniently used for X-ray diffraction studies. Figure 5 shows a schematic diagram of the circuit and the arrangement of accessories. This unit is a slight modification of a prototype used in the study of Ti-Fe and Ti-Ni alloys.[2]

The furnace tube is ½-in. diameter standard vycor tubing 15 in. long. The tube and heating element are enclosed between two insulation bricks. The element consists of two 24-gage alumel wires connected in parallel and insulated with porcelain tubes. Current control is achieved by means of a variable transformer.

Since titanium and zirconium react with SiO_2 at 1000° C, it is necessary to use molybdenum boats as specimen containers. When the furnace is charged and ready for operation, the system is evacuated to about 10^{-4} mm Hg and the charge is heated either in a vacuum or in an inert gas atmosphere. It is possible to heat to 1000° C in one to two minutes. Quenching is performed by introducing a blast of purified helium gas through the two-way valve at one end of the furnace tube. A Pyrex stopcock has been found to operate satisfactorily as a gas stop. If an inert atmosphere is used in the furnace during heating, then the furnace tube should be evacuated immediately prior to quenching.

During quenching, the molybdenum boat and powder specimen are simultaneously projected from the hot zone of the furnace and are cooled by the gas flow. The quenching rate for a small sintered charge is estimated to be in excess of 500° C per second. In some cases, depending on the metal and the holding temperature, the powder specimen may not sinter, and in this case the quenching rate will be considerably faster. The specimen and molybdenum boat are retained in the vacuum flask which is connected to one end of the furnace tube and to the vacuum pump. (See Fig. 5.)

It is essential that the system be capable of reaching and holding a vacuum of 10^{-4} mm Hg. The helium gas should be passed through activated copper gauze at approximately 500° C to remove oxygen. More efficient purification can be achieved by using a hot calcium train at 650° C to remove oxygen and nitrogen and another calcium train at 350° to remove hydrogen from the gas.

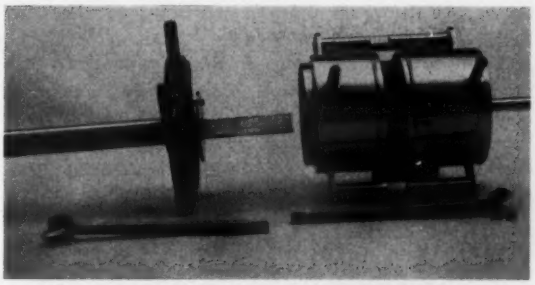

FIG. 7. HIGH-TEMPERATURE ATTACHMENT FOR THE NORELCO X-RAY DIFFRACTOMETER

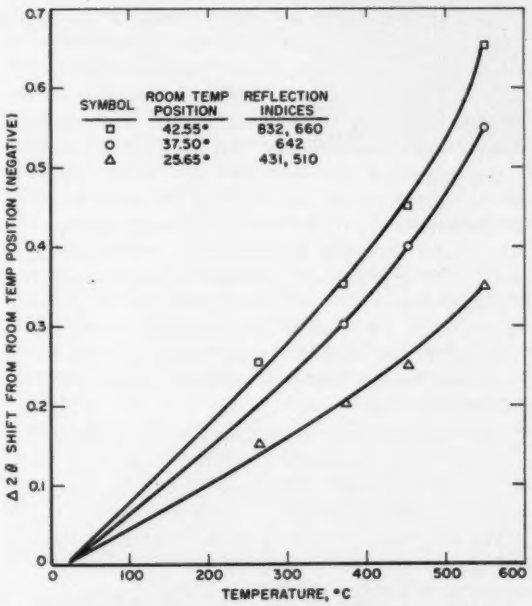

FIG. 8. CHANGE IN ANGLE OF THE DIFFRACTED X-RAY BEAM FOR THREE IMPORTANT DIFFRACTION PEAKS OF DELTA PHASE IN 32.6% TIN ALLOY OF COPPER-TIN

This unit has been used successfully in several research projects including Ti-Cu and Cu-Si phase-transformation studies. Its principal advantages include the extremely rapid heating to temperature and relatively easy recovery of the powdered material from the vacuum flask even if the charge is unsintered.

X-Ray Goniometer Attachment

The constitution of alloys at elevated temperatures is frequently reported in the literature on the basis of specimen structures examined after quenching to room temperature. In such studies it is possible that transformations may have occurred by shear or diffusion during cooling. Consequently, in order to

determine the true phase constitution of alloys at high temperatures (e.g., 1000° C), it is necessary to make direct observations or measurements at the temperatures involved. A high-temperature goniometer attachment for the Norelco X-ray diffractometer unit was constructed as part of a recent research project of the Metallurgical Division. Financial assistance for this project was provided by a grant from the Agnes H. Anderson Fund. The unit has been designed for possible operation in the temperature range below 1000° C. The present design is a modification of the attachment reported by Butters and Parr.[3]

Figures 6 and 7 show the features of the goniometer attachment design. The unit is mounted on a hollow stainless steel shaft which replaces the regular shaft of the goniometer. The shaft also acts as the vacuum line to the furnace and holds the specimen plate in a precise position. An aligning adjustment is positioned on the shaft and locates the plane of the half-diameter of the shaft in the zero plane of the goniometer for critical specimen adjustment. The base or head of the attachment is machined from ⅜-in. copper plate and contains a machined groove for an O-ring seal contact with the can or cover of the furnace. A kovar thermocouple terminal is mounted in the head, and water cooling is provided by copper tubing which is soldered to the head as indicated in Fig. 6.

The can or cover of the unit is a double-walled container with a window provided to allow passage of the incident and diffracted X-ray beams. The space between the container walls serves as a water jacket for effective cooling of the assembly. Copper end plates have been soldered to the double-walled assembly to enclose the water jacket.

The furnace heating element support consists of a 1⅜-in. diameter tube of zircon-mullite vitreous refractory which is fastened in position inside the can. Each end of this tube is slotted for spacing the 24-gage Pt 20% Rh resistance wire heating element. The element is wound longitudinally about the inside surface of the refractory core. The heating element support is surrounded by a coaxial stainless steel radiation shield and the ends are shielded by stainless steel disks.

Mounting guides have been provided on the outside of the container to facilitate easy and accurate mounting of the container on the head of the unit without damaging the specimen plate. The specimen plate used in the present unit consists of ⅛-in. thick vitreous alumina. It is mounted in a cantilever position to the head of the unit, and when the can is in position the specimen plate is surrounded by the heating element. For high-temperature studies of reactive metal specimens, a sheet of molybdenum is placed on the specimen plate to prevent contact between the metal and the refractory.

The window of the attachment is covered with aluminum foil which is clamped and sealed to the outer surface of the can to provide a vacuum seal. The specimen temperature is measured by a thermocouple which is in direct contact with the powder on the specimen plate. This method proved to be satisfactory in the earlier design of Butters and Barr.

A number of tests have been conducted with the furnace attachment. Most high-temperature runs have been made with a helium atmosphere rather than in a vacuum, although a pressure of 0.1 micron is obtainable. Specimen temperatures up to 970° C have been achieved very easily. This limit was imposed by the autotransformer which was used for current control, but the furnace is capable of higher temperatures. High-temperature studies have been conducted on several selected alloys of the Cu-Sn system. The angular shifts of three diffraction peaks of the delta phase (32.6% Sn) have been measured up to 529° C and are plotted in Fig. 8. Data of this type are valuable in estimating thermal expansion coefficients.

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ACKNOWLEDGMENTS

The authors wish to acknowledge the contributions of J. Daub and M. P. Gomez to the design and construction of the quenching furnaces and high-temperature X-ray equipment. The data plotted in Fig. 8 were obtained by G. A. Dreyer and T. J. McCann.

EXPANDING MINERAL RESOURCES

(Continued from page 1)

natural abrasives, emery, corundum, and garnet. Recently, industrial diamonds, piezoelectric quartz and insulating mica have been made; these are high value minerals and susceptible to manufacturing in competition with the natural materials. For high-temperature applications new metallic oxides singly or in alloyed systems are being developed. Ceramic materials compounded from natural minerals have been in the past the common refractory materials; manufactured compounds have now entered commerce, and a study of the physical characteristics of all these materials is engaging the attention of more and more ceramists. This activity will broaden the range of use for the non-metallics and also substitute for and supplement the scarcer metals.

The storehouse of natural resources has many rooms. Each may be unlocked by research and the door to yet another room disclosed. The certain exhaustibility of today's deposits is offset by new discovery, new technology, and new understanding. The primary purpose of the School of Mineral Engineering is to develop men to work, to inquire, to venture in the many rooms of our mineral storehouse. The reports in this issue of *The Trend in Engineering* reflect some of this work.

REFRACTORY CERAMIC COATINGS

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Refractory ceramic coatings for metals have come into prominence just within the last few years; only a limited number of investigations pertaining to them were carried on prior to 1947. They are of interest owing to the abrupt changes in material requirements brought about by the "jet age." Although other industries are vitally concerned with developments in ceramic coatings it has mainly been in response to the needs of the aircraft industry that investigations in this field have been undertaken. A considable amount of basic research has been instituted in universities and various industries by the Air Force and other government agencies, and in the material developmental centers of various government installations.

Ceramic coatings are required primarily for heat- and corrosion-resistance purposes although numerous other properties are also essential. Prior to the early postwar years (1947-1949) highly refractory ceramic coatings had been neglected for two major reasons: materials then in use had adequate physical characteristics (corrosion resistance, etc.) to meet the requirements of the pre-jet age; the original standard refractory coatings were still suitable for low-temperature resistance.

Although the development of "super-alloys" relieved the need for ceramic coatings to a large extent, the new temperature ranges created by supersonic and hypersonic speeds called for a development of ceramic coatings for application to the super-alloys.

The search for new materials has been approached from several directions, among which the following may be listed:

1. to alter or change designs where possible so that high temperatures are not encountered,
2. to develop new alloys which have sufficient strength at elevated temperatures,
3. to develop insulating ceramic coatings which will reduce temperatures of the metal to such a degree that they have sufficient strength,
4. to develop other types of coatings and surfaces, especially metal coatings applied by electroplating, metalizing, and other means.

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The first solution is obviously the most expedient in most cases since new materials would not have to be developed, but in many design problems high-temperature contact presents an unalterable condition. The fourth avenue of approach has shown insufficient promise to date. Research is currently being directed essentially to the second and third alternatives with the third alternative showing greater promise of success in the immediate future.

Depending on the particular requirements which the ceramic coating must serve, the specifications will vary. For example, the coating might be subjected to various atmospheres, or it might be subjected to sustained high temperatures or extreme temperature gradients. In general, however, the characteristics which are sought in a refractory ceramic coating are the following: chemical resistance at elevated temperatures; high reflectivity or high emissivity; surface hardness with good erosion resistance, abrasion and friction resistance at elevated temperatures; vibration resistance; and heat insulation.[1]

Solution Coatings

Ceramic coatings may be applied in a variety of ways. One of the easiest methods of application is utilized in applying a true solution ceramic coating. This may generally be described as an inorganic, nonglassy coating which is usually applied by spraying a heated surface with a true solution.[2] The coatings which have been used with most success are the refractory oxides of zirconium, chromium, titanium, cerium and magnesium. Since solution ceramics are deposited from true solutions, the rate at which they are applied can be accurately controlled by simply controlling the concentration of the solution. This allows coats of infinitesimal thickness to be deposited from very dilute solutions.

One of the characteristic properties of solution ceramic coatings is the diffuse X-ray and electron diffraction patterns which they exhibit. This does not mean that the coatings are amorphous, but only that the crystallites developed are too small and disoriented to produce definite crystalline patterns. If

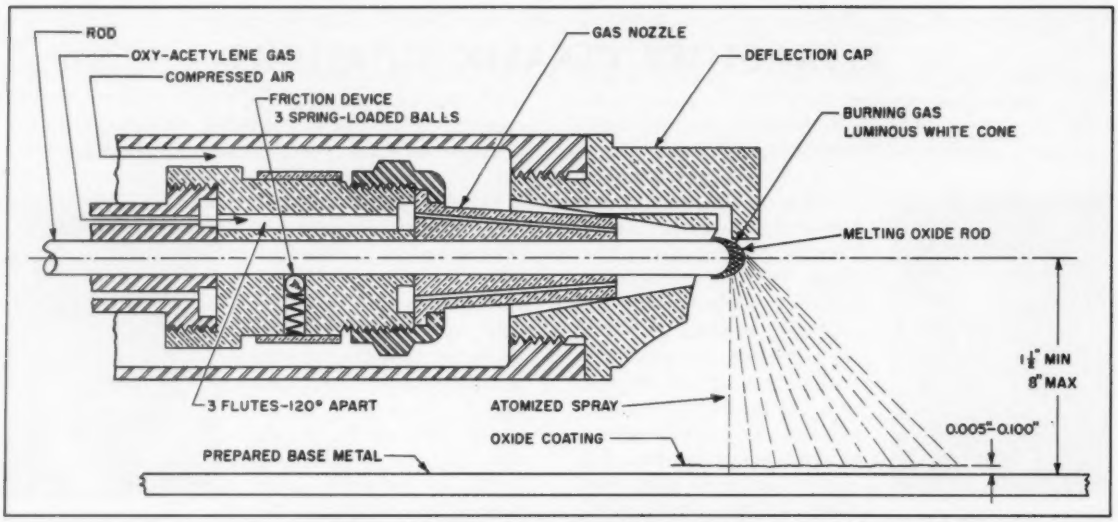

FIG. 1. DIAGRAM OF A FLAME-SPRAYING GUN *Courtesy of* CERAMIC INDUSTRY

the coatings are held at sufficiently high temperatures for crystal growth to occur, the characteristic diffraction pattern of the crystalline material is developed.

Although their individual properties differ, solution ceramics have many characteristics which are due in large extent to the method of application. All of the solution ceramic coatings are of relatively low density. This low density probably contributes to their good thermal insulating properties. As a group, solution coatings have a marked resistance to corrosion. When the corroding medium is a molten metal or viscous glass some of the coatings display outstanding resistance to attack. This protection is attributable to the high insulating nature of solution ceramics and to the high surface tension and viscosity of the molten materials. In some cases the coatings must be overlaid or modified with other materials to qualify as truly protective coatings. A promising attribute of these coatings is the relative ease with which they may be coated or impregnated with other materials. Thus, metallic or inorganic precipitates may be added to the solutions or applied in subsequent coatings. Since the coatings are not bonded by valence forces to the base material, the adherence of a coating is relatively independent of the material to which it is applied. The application temperature of the material is usually 400-700° F, but adherent coatings have been obtained at temperatures as low as 300° F and as high as 1200° F.

The possible uses of this type of refractory coating are quite varied. They may be used for upgrading the surface properties of refractory enamels or materials such as carbon and graphite. They may also be used as a base-coat substitute for enamels and glazes. They may protect soft or light metals against radiant heat, or prevent contact with molten metals or reactive solids. They often form an excellent base for many flame-sprayed ceramic coatings on light metals.

Flame Spraying

The method of flame-spraying a coating allows refractory oxides with high melting points to be applied to a variety of different substrates. The technique consists of introducing an oxide into a high-temperature flame, melting it, and projecting the molten droplets onto the surface of the metal to be coated. The refractory oxide can be introduced as a powder or in the form of a solid rod. As the material is fed into an especially designed torch it melts, and compressed air at a pressure of approximately 70 to 90 psi projects the molten particles onto the prepared surface. Figure 1[3] shows a specially adapted metallizing gun for the application of flame-sprayed ceramic coatings with a preformed rod as the source of the refractory material. Almost any material which will melt rather than sublime, and any which will form droplets rather than fibers (thus excluding glass), can be applied by spraying.[4] Figures 2 and 3 show pieces which have been flame-sprayed with ceramic coatings. Figure 4 shows how the coating is applied by a flame-spraying gun.

Another limiting factor is the chemical reactivity of the compound with the high-temperature flame. An oxyacetylene flame is generally highly oxidizing, and if compressed air is used for projecting the liquid particles onto the metal surface the chances for oxidation are still greater.

To date, aluminum oxide, zirconium oxide, and zircon ($ZrSiO_4$) coatings have proved to be the most successful for flame-spraying, although some other

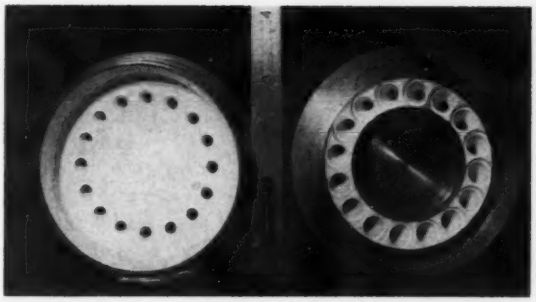

FIG. 2. EXAMPLE OF SMALL PART FLAME-SPRAYED WITH 0.010-INCH COATING

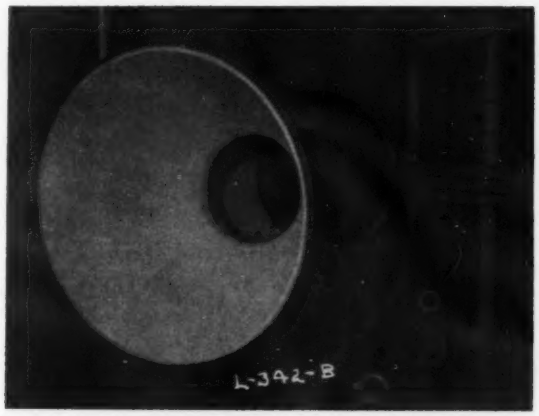

FIG. 3. ROCKET NOZZLE FLAME-SPRAYED

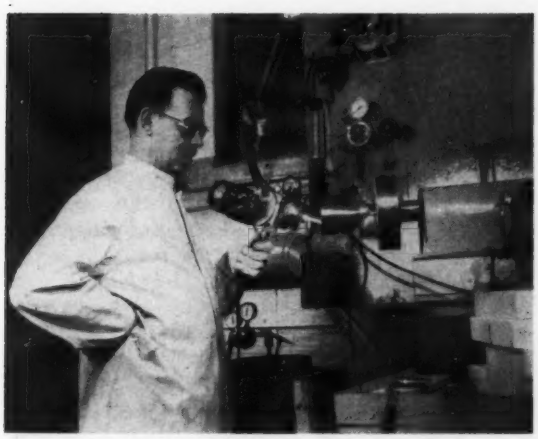

FIG. 4. APPLICATION OF FLAME SPRAY

Note: Figures 2, 3, and 4 are reproduced by courtesy of the Norton Company, Worcester, Massachusetts.

complex oxides have been investigated. Table I shows some properties of these materials.[5] Suggested applications for these coatings are numerous; only a few which have shown exceptional promise are listed here:

Rockets: nozzles, motor tube linings, thermal barriers;

Missiles: vanes, skin protection, motor components;

Ram jets: tail-pipe lining;

Gas turbines: inner combustion chamber lining, cross-fire tube lining, flap nozzle coating, housing and shroud ring insulation;

Miscellaneous: burner parts protection, electrical insulation, thermocouple tube protection.

As an example of the thermal insulative properties of these coatings, a maximum temperature drop of 1500° F has been reported through a 0.010-in. thickness of Al_2O_3 by a manufacturer of power plants for guided missiles. This material has also been reported as useful with both solid and liquid propellants, and capable of withstanding erosive and corrosive conditions in nozzles for high velocity reaction motors.[6]

Vitreous Coatings

Although the previous discussion has dealt exclusively with crystalline coatings (excepting a minor quantity of a vitreous phase inherent in applications of zircon) a variety of compositions with a predominant vitreous phase are available for many useful applications. Many of these are patterned after National Bureau of Standards compositions and are primarily alkaline earth-borosilicate glasses. They also usually contain large quantities of aluminum or chromic oxides to increase their resistance to elevated temperatures. These are designed primarily to improve the oxidation resistance of base metals up to 2100° F. When required they can be made to provide resistance to abrasion, corrosion, and galling. By varying the compositions a wide range of base metals and operating conditions can be utilized.

One coating of particular current interest is a barium-beryllium silicate glass, free of alkalies and boron for use in nuclear reactors. Designated composition N-143 by the Bureau of Standards it was designed for alloys such as type 310 stainless steel, Inconel, and Nichrome V, and provides oxidation protection up to 2050° F. One of its major properties is its low absorption coefficient for thermal neutrons.[5]

Applications for high-temperature vitreous coatings are numerous. On low carbon and low alloy steels they are used on such equipment as space heaters, heat exchangers, combustion chambers, and exhaust pipes. On stainless steel they find application in turbojet combustion chamber liners, tail cones,

TABLE I

PROPERTIES OF REFRACTORY OXIDE CERAMIC COATINGS [a]

	Aluminum Oxide	Zirconium Oxide	Zircon	Aluminum Silicate	Titanium Dioxide	50% Iron Titanate: 50% Gamma Alumina	Iron Titanate	Rare Earths (50%CeO_2)
Application Properties								
Deposition Rate (sq ft/hr/10 mils)	15-16	4-10	....	16	10	10	10	8
Thickness Range (mils)	5-50[b]	5-50[c]	5-50	....	....	....	....	....
Finish After Polishing (μin. rms)	2-50[d]	15-50[d]	30-50	52-77	6-43	16-38	7-52	32-48
Thermal Properties								
Melting Point (°F)	3600-3700	4500-4600	3000	3200	3200	2500	2500	....
Coeff. of Thermal Exp. ($\times 10^{-6}$/°F)	4.0-4.3[d]	5.4-6.4[d]	4.2	2.5	4	....	....	5
Thermal Conductivity (Btu-in/hr sq ft °F)	19-20	7-8	15	25	45	....	....	20
Shock Resistance	Good	Very Good	Good	....	....	....	....	....
Other Properties								
Dielectric Strength (v/mil)	200	100[e]	Nonconductive	....	Conductive	Conductive	Conductive	....
Vickers Hardness (DPH, 25-g load)	1400	400	1000 Knoop	650	1500	800	700	600
Porosity (%)	8-12	8-12	8-12	....	....	....	....	....
Density (lb/cu in.)	0.12	0.19	0.14	....	....	....	....	....

[a] Properties generally apply to flame-sprayed coatings. Properties of solution coatings may differ somewhat.
[b] Thicknesses up to 0.125 in. can be produced for special applications.
[c] Thicknesses over 0.10 in. can be produced for special applications.
[d] Varies with method of application.
[e] Nonconductive at room temperature; conductivity increases rapidly above 2190° F.

and afterburner liners, and in industrial uses such as furnace baffles, combustion chambers, and electric heating elements.

New formulations for coating aluminum extend its useful life to temperatures of 1500 to 1550° F before softening occurs, even though melting points of aluminum and its alloys are in the range of 1250 to 1350° F. The coating is usually applied in thicknesses of 0.0015 in. on one or both sides of the metal to provide a rigid system. The coating is composed of three prime components: a low melting glass, refractory additions of TiO_2, MgO, or SiO_2; and fluxing agents, usually lithium compounds.

An indication of the refractory properties of such coatings is evidenced by flame impingement tests on coated and uncoated specimens. Tests have shown that a direct flame could burn through an uncoated specimen in 30 to 45 seconds (depending on the alloy and thickness thereof), while the coated specimens withstood the flame at least six hours without failure.[7]

One approach to the problem of reducing the temperature of metals (such as an afterburner shroud) during operating conditions has been the application of two different types of ceramic coatings, one on the heated side, the other on the relatively cooler side. Taking advantage of the inherent emissivities of the coatings, a highly reflective coating, e.g., flame-sprayed aluminum oxide, could be applied to the higher temperature side to reflect as much heat as possible. A dark coating with high emissivity, e.g., one containing nickel and chromic oxides and having an emissivity of 0.95 at 1500° F, applied to the opposite side would absorb heat from the metal, thus acting as a thermal transmitter.[5,8]

Coatings for Graphite

Graphite has several outstanding properties which make it very desirable for use at high temperatures. However, its resistance to oxidation is poor and it is relatively soft, thus imposing the need for its protection before it can successfully withstand service in many applications.

One coating which has been investigated is molybdenum disilicide. Dispersed in a resin vehicle it forms a hard, adherent, glazelike coating on graphite when heated to high temperatures in neutral or reducing atmospheres. It provides considerable protection when in contact with high-velocity, hot, oxidizing gases, conditions which would be encountered in rocket exhausts. The upper use limit under oxidizing conditions is 3500° F.[9,10]

Another coating which has been evaluated is a pure, self-bonded silicon carbide coating. The coating is actually formed by a high-temperature chemical reaction, causing it to be an integral part of the graphite. Since the coating constitutes only a thin layer (0.003 to 0.020 in. thick) the graphite retains

most of its inherent properties, including low density. The maximum operating temperature of the coating varies, but temperatures in excess of 4000° F have been resisted in some cases.[10,11]

Cermet Coatings

Cermets are composite materials which are designed primarily to maintain strength properties at elevated temperatures. This is accomplished by making a duplex body composed of metal and ceramic components which utilize the refractory properties and oxidation resistance of the ceramic phase and the ductility and flexibility of the metal phase. Although cermets have been used alone for the most part, it is also possible to utilize them as coatings for a variety of substrates in special applications, primarily under conditions of severe abrasion.

While they can be incorporated in a vitreous matrix as a refractory phase, they are more often applied by a process known as flame-plating. The cermet used most often to date is tungsten carbide, although other compositions, including oxides, can be applied by this process.

The flame-plating process involves the use of a specially constructed spray gun in which the cermet is fed into its chamber and suspended in a mixture of oxygen and acetylene. When this mixture is ignited a detonation occurs. The detonation wave travels through the gun barrel at ten times the speed of sound with a consequent heating of the particles to a plastic state. The particles embed themselves on the substrate where a microscopic welding action takes place producing a very strong bond. Although temperatures inside the gun may reach 6000° F, the temperature of the part being plated seldom exceeds 400° F; thus there is little chance that it will warp or that its physical properties will change. Coatings can be applied in a thickness range from two to ten mils. Although the as-coated surface condition is rather irregular, standard diamond-finishing methods can produce a surface finish of 0.5 microinch rms.[12,13]

Summary

In the short period of time during which ceramic coatings have been available, remarkable progress has been made in their development and applications. They have extended considerably the useful range of low-cost metals, making them available under conditions which they could not begin to approach in an uncoated state. Also they raise the temperature limit of premium alloys. Not only do they provide a hard and abrasion-resistant surface, but they also protect the metal from corrosion and other types of chemical attack.

Only a general indication of formulations has been given here. For specific applications it is usually necessary to adjust the compositions somewhat in order to obtain proper coefficients of thermal expansion, viscosity, surface tension, hardness, etc. It is reasonably safe to state that a ceramic coating can be obtained for almost any metal substrate. It should be recognized, however, that ceramic coatings cannot be "bought from the shelf," as it were. Because of the extreme variety of coatings that are available, is is difficult for the designer, working on his own, to select the best coating to meet a particular set of conditions. The best choice is usually made by mutual agreement between the designer and material supplier.

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REACTOR REPORT OFF PRESS

Report No. 7 of the Engineering Experiment Station, "A Natural Uranium-Graphite Subcritical Reactor System for Education and Research," has just been issued. Part I, "Description and Experimental Measurements," by A. L. Babb, L. Grimsrud, and W. E. Wilson, is a revised version of a report (A/CONF. 15/P/1082) presented at the Second United Nations Conference on the Peaceful Uses of Atomic Energy, held at Geneva, Switzerland, last September.

Authors of Part II, "IBM 650 Computer Programs for Effective Size, Diffusion Length, and Material Buckling Calculations," are A. L. Babb, L. Grumsrud, and S. Tashiro.

Dr. A. L. Babb, Associate Professor of Chemical Engineering, is in charge of the Nuclear Reactor Laboratory of the University.

X-Ray Spectroscopic Analysis of a Slag-Metal System

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Quantitative analysis is one of the major difficulties in the study of slag-metal systems. The study usually concerns itself with the distribution of a compound or element between these two immiscible molten phases. Normal chemical analysis carried out by an experienced chemist is probably the most accurate method, but this is time consuming and expensive. X-ray spectroscopic analysis offers a quick, accurate, and inexpensive method of analysis, if the necessary equipment is available.

X-ray spectroscopy is based on simple phenomena. When a sample is bombarded by high-energy X-rays, these primary X-rays knock out the lower energy, inner electrons of the sample atoms. The electrons in the higher energy shells then drop down into the inner shell. When this happens, secondary X-rays are emitted by the atoms of the sample. The wave length of the secondary X-rays depends on the structure of the atom bombarded. Their intensity depends on the intensity of the primary X-ray bombardment and the type and number of atoms present. If a system can be devised to measure the wave lengths and intensity of the secondary X-rays emitted by the sample, it is possible to get both a qualitative and a quantitative analysis of a sample.

There are, however, complicating factors. The analysis of a sample for copper will be used to illustrate such complications, since the latter part of this paper deals with a copper analysis. In the first place, a number of elements present in a sample can cause what is called the interelement effect. When this occurs, the secondary X-rays from one of the other atoms has just the right energy to knock free the inner electrons of copper. The intensity of copper radiation is then no longer a function of the number of copper atoms present and the intensity of the primary radiation. It is also dependent upon the number of atoms of the element causing the loss of additional electrons. The more of these atoms that are present, the greater the intensity of the copper radiation.

A second complicating factor results from variations in the intensity of bombarding X-rays. Since most analytical procedures are used over a long period of time, it is difficult to set the X-ray equipment so that the primary radiation has precisely the same intensity each time a sample is analyzed. If it were not for this factor, making a sample analysis would be extremely easy. One would only have to prepare samples containing known quantities of copper, measure the intensity of radiation emitted from these and plot a reference curve of the percent copper versus intensity of secondary copper radiation. When the intensity of radiation from an unknown is then measured, the percent copper can be obtained directly from the curve. However, the use of such an analytical curve obviously requires that the intensity of the bombarding X-rays used for both the known and unknown samples be identical.

E. C. Roberts

The use of a standard element overcomes this last source of error. An element whose characteristic secondary radiation has a wave length close to that of copper can be added to the samples in a fixed quantity. Then a ratio of intensities is used. The ratio of the copper intensity to standard element intensity is a function only of the percent copper in the sample. Any variation in primary radiation will affect both the copper and the standard. A plot of intensity ratio versus percent copper can then be used as the analytical curve. Figure 1 is an example of such a curve.

Slag-Metal System Analyzed

The analytical technique worked out in the research described in the remainder of this paper is one used to find the distribution of copper between molten lead and a liquid PbO-SiO_2 slag. This particular slag-metal system is of interest to the Department because it is used in an experiment conducted in the metallurgical thermodynamics laboratory. What is needed for this experiment is a quick, accurate quantitative analysis of copper in the slag and the metal.

The actual laboratory experiment is quite simple. Clay crucibles containing PbO, SiO_2, a reducing agent (flour), and varying amounts of Cu_2O are

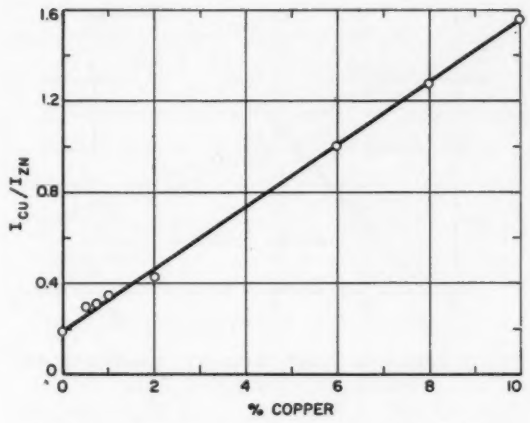

FIG. 1. PERCENTAGE COPPER IN ALLOY VS. I_{Cu}/I_{Zn}

heated in a muffle furnace to 950° C. The flour reduces a portion of the PbO and the remainder reacts with the SiO_2 to form a slag over the molten lead. Copper oxide is also partially reduced and this copper distributes itself between the slag and the metal. When equilibrium is obtained, the cooled slag and metal are analyzed for their respective copper contents. These data, plus information on the activity of copper in the Cu-Pb alloy, can be used to calculate the activity of copper in the slag and to determine the molecular association of SiO_2 and PbO in the molten slag.

Analytical Technique Used

The analytical curve for X-ray spectroscopy was prepared from samples of known concentrations containing a standard element. In this project such a curve had to be prepared for a series of slags and another one for a series of Cu-Pb alloys. The analytical method applied to this investigation differed from the normal procedure in its use of an external standard. Usually an internal standard is used by mixing directly into each sample a chosen reference material in a fixed percentage. That is, one gram of powdered standard element is added per so many grams of sample. The same percentage is added to the knowns and to the unknowns. In the external standard method, a solid piece of the standard element is mounted permanently in the sample holder used for the analysis. This same piece of standard is present each time an analysis is conducted.

The major advantage of the external standard is obvious. No weighing or mixing is necessary. The only preparation required for an unknown but representative sample is to reduce it to particles of sufficiently small size before loading it into a sample holder. There are, of course, disadvantages or certain precautions necessary and these became obvious as the technique was developed.

Zinc was selected as the external standard material; thus the copper radiation intensity was compared to that of a fixed piece of zinc. As it happens, the choice of zinc has a special advantage. Zinc secondary radiation has just the right energy to knock out the inner electrons of the copper atoms. Therefore, the secondary radiation from copper is enhanced, making it possible to detect very small percentages of copper. Since the amount of zinc present does not change, the interelement effect is an advantage in this analysis.

Procedure

Many of the procedures used in the early part of the project were dropped as being unsatisfactory. Only those which were retained in the final method of analysis will be reported here.

The metal standards, in which the percent copper was known, were prepared from pure assay test lead and chemically pure copper powder. These standards were melted under a cover of carbon and then cast in a cast-iron mold. The metal sample removed from the mold was filed into fine particles.

The oxide slag standards were prepared from chemically pure PbO, SiO_2, and Cu_2O. The PbO-SiO_2 slag was assumed to be $2[(PbO)_2\ SiO_2]$. Therefore, a master synthetic slag was prepared by mixing PbO and SiO_2 at the weight ratio dictated by this assumed molecular association. Three independent sets of slag standards were prepared. The method used in preparing the A series was unsatisfactory owing to the absorption of moisture during weighing. The B series was prepared from PbO and SiO_2 under conditions which excluded moisture accumulation. The PbO, SiO_2, and Cu_2O were tumble-mixed prior to use. The C series was prepared by fusing the PbO and SiO_2 to a synthetic slag, cooling, crushing, and drying. Cu_2O was then added to portions of this master slag to give the desired range of copper percentages. These were then tumble-mixed, and ground in a mechanical mortar and pestle.

Slag-Metal Equilibrium Experiment Samples

A series of unknown slags and metal buttons were prepared by carrying out the laboratory experiment. Eight fire clay crucibles were each filled with 120 g of PbO, 10 g of SiO_2, 5 g of flour, and unit increases of from 1 to 8 g of Cu_2O. These were fired in the muffle furnace for 30 minutes at 950° C. The cooled slags were first crushed to -65 mesh and then treated as described later. The metal buttons were filed in the same manner as the metal alloy standards.

Sample Mounting

The sample holders used in this project are of special interest. Since an external standard was used, it was necessary to mount the zinc directly in the

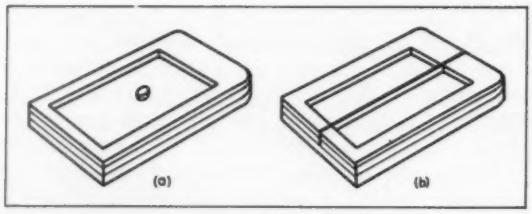

FIG. 2 SAMPLE HOLDERS

(a) With zinc button standard. (b) Final model with 0.013-in. strip zinc standard for slag and 0.020-in. strip zinc standard for alloy.

holder. First, a small round button of zinc was mounted in the center of the holder (Fig. 2-a). This device was unsatisfactory because slight differences in the location of the zinc button caused extreme differences in the intensity of emission from the zinc. In a second approach (Fig. 2-b), a thin ribbon of zinc was mounted edgewise down the middle of the holder. This was much less sensitive to holder location.

Preparation of the Analytical Curves

The X-ray equipment used in this project was a Norelco X-ray spectroscope with a NaCl analyzing crystal and a scintillation counter. All samples were radiated with unfiltered X-rays produced by a tungsten target tube operating at 30 KVA and 30 milliamperes. In the early exploratory work, including locating the best peaks, testing various holders, and checking purity of material, the Brown strip chart recorder was used. The final preparation of the analytical curves was done by the more accurate fixed count method, using either 25600 or 12800 counts. For most of the measurements the former figure was used. The voltage applied to the scintillation counter was set at 1155 v, which by trial gave the best peak to background ratio for the CuK_α radiation.

Discussion of Results

Many techniques had to be developed in this investigation before reliable data could be obtained. Five important experimental considerations were revealed. These will now be considered individually in some detail.

Holder Location. Figure 3 shows the effect of the change in holder location on the zinc intensity. As it happened, the holder was first arranged with the button in an extremely critical position. The movement of the holder 1 mm "in" gave practically no zinc emission and the movement 1 mm "out" gave nearly double the normal intensity. Considerable work had been done before this fact was realized. The construction of a sample holder having the zinc strip down its entire center line removed this source of error. (See Fig. 2-b.)

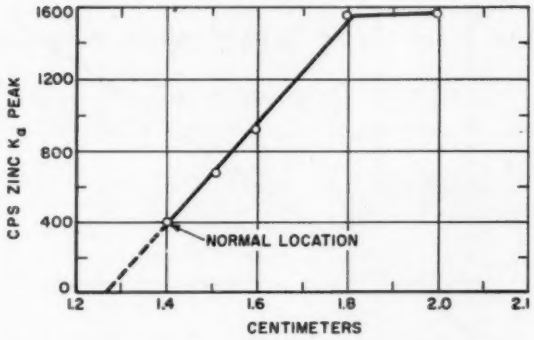

FIG. 3. EFFECT OF SAMPLE-HOLDER PLACEMENT ON THE INTENSITY OF THE ZnK_α PEAK

Emission Peaks Measurement. The early data reports include the intensity of four lines CuK_α, ZnK_α, ZnK_β, PbL_α. The ratios of CuK_α and ZnK_β were nearest unity in the range of copper concentration encountered in this project. This ratio when plotted against copper concentration gave the most satisfactory results, so the measurement of other lines was stopped. All curves plotted were on the basis of this ratio. Portions of each sample were loaded at least three times, and when results seemed erratic, up to ten loadings were counted.

It must be noted, further, that these curves are based on the total intensity of the peaks, not on the intensity above background. This explains why the I_{Cu}/I_{Zn} ratio does not go through zero at zero percent copper. The intensities were measured in this way in order to keep the procedure as simple as possible. Thus a large number of samples could be analyzed in a short time. This method sacrifices some accuracy, but the nature of the results required and the speed of this method make it satisfactory.

Packing Sample Holder. The intensity of copper radiation from the slag standards can be increased relative to that of the zinc by forcing about half again as much sample into the holder. The second group of data for the B series was taken with 4.2 g of standard sample packed into the holder. These are the data used in Fig. 4.

This effect appears to be due to the use of an external standard. If an internal standard had been used, there would have been an increase in the amount of zinc as the sample was pressed into the holder. Using an external standard, the quantity of zinc was fixed, and packing only increased the copper present. This effect was not found in the case of the alloy samples, for hand pressure could not cause the filings to compress in the holder.

The B series of standard slags were loaded at 4.2 g per loading because it was found that the experimental slag, crushed to -65 mesh and loaded by

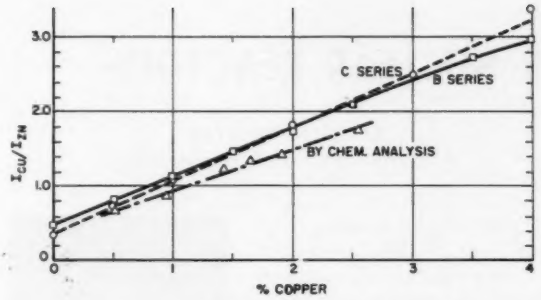

FIG. 4. PERCENTAGE COPPER VS. I_{Cu}/I_{Zn} IN SLAGS

filling the holder and scraping it off level, gave an average of 4.2 g per loading. The B series, scrape-loaded, averaged 2.1 g per loading. The C series, made up later in the investigation, averaged 3.9 g. Figure 4 (I_{Cu}/I_{Zn} vs. % Cu) shows that the B series packed and the C series normally loaded gave nearly the same ratios.

X-Ray Analysis and Chemical Analysis. After the intensity ratio versus percent copper curve was prepared for slag using the B series standards packed at 4.2 g per loading, the experimental slags were run and the intensity data used to get the percent Cu in these unknowns. As a check on the procedure three of the experimental slags were sent out for chemical analysis. The results were not at all in agreement with the X-ray analysis, as can be seen in Fig. 4 (I_{Cu}/I_{Zn} vs. % Cu in slags).

Further samples were chemically analyzed, both experimental slags and C series of slag standards. The chemical analysis of the B and C series was in close, but not perfect, agreement with that predicted by the mixing weights. One or two samples showed a lower percent copper by chemical analyses. The additional experimental slags reported a larger copper content than that indicated by the X-ray analyses.

This discrepancy had to be explained before the slag curve could be used. The first suspected source of error was the interelement effect of lead. The lead content of the actual experimental slags was slightly different from that of the standard samples. A series of synthetic slags were prepared in which the percent copper was fixed and the percent lead varied from 45 to 75. There was a marked effect on the copper-to-zinc intensity ratio, which decreased as the lead increased. The change due to the small difference in the lead content of the actual slag and synthetic standard slags was not enough, however, to account for the error; further, it was changing the ratios in the wrong direction.

Particle Size. The other major difference between the standard slags and the experimental slags was particle size. The standards had been mixed and crushed in a mechanical mortar and pestle and were

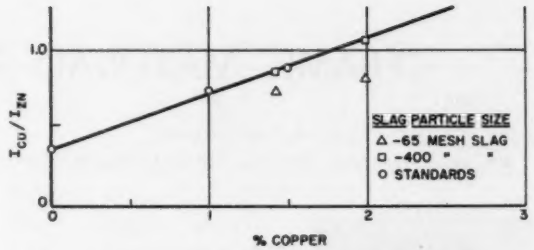

FIG. 5. PERCENTAGE COPPER VS. I_{Cu}/I_{Zn} SHOWING EFFECT OF PARTICLE-SIZE VARIATION IN SLAGS

very fine. The experimental slags were X-ray analyzed in the -65 mesh condition. Two of the experimental slags were cut into two portions. One-half was left as -65 mesh and the other was crushed in the mechanical mortar until its fineness was equivalent to that of the standard slags. These slags, along with the only standards still available in the copper percent range of the experimental slags, were dried overnight at 105° C and then X-ray analyzed with the holder carefully packed with 4.1 g of sample.

Figure 5 (I_{Cu}/I_{Zn} vs. % Cu in slag) shows the result of the particle-size variation in the experimental slags. The increase in the intensity ratio is due entirely to an increase in the intensity of the copper emission as the particle size is reduced. The zinc intensity stayed nearly constant.

Conclusions

A satisfactory X-ray spectroscopic analysis was developed by which the percent copper in a PbO-SiO_2-Cu_2O slag and in a Pb-Cu alloy, which had been in equilibrium, could be determined.

An external standard technique was used, which requires several precautions if accurate results are to be obtained:

1. The standard must be mounted in a manner that prevents variation in amount of standard exposed to the primary X-rays.
2. When a material can be packed in the holder, the weight of the sample in the holder must be the same in all loadings.
3. If fine crystalline material is used in preparing the standard samples, the unknowns must be reduced to nearly the same fineness if they are to respond in the same manner to the X-rays.

The use of an external standard and fixed counting of total peak intensities has two advantages:

1. No close tolerance sample weighing is necessary. The only requirement is a uniform technique of loading the sample holder.
2. The analysis is rapid, requiring only the counting by the fixed count method of two peaks on each sample loading.

(Continued on page 32)

CERAMIC MATERIALS FOR NUCLEAR REACTORS

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Nuclear reactors have offered an unusual challenge to the materials engineer because of the restrictive parameters required by their design criteria. The materials must satisfy ordinary requirements such as strength, refractoriness, heat transfer, and corrosion resistance, in addition to those properties which are peculiar to the nuclear field. The latter include resistance to radiation damage, suitable neutron source, and the appropriate absorption cross section and scattering characteristics for thermal neutrons.

Since the desirable spectrum of such properties is, for the most part, inherent in many ceramic materials, the use of ceramics in the design and construction of many reactors has become a necessity.

In this discussion consideration must be given to the type of reactor as well as the purpose for which the material is to be used.

Fuel Elements

Materials to be used in fuel elements must, of course, be fissionable. To obtain the maximum in thermal efficiency which requires that fuel materials withstand higher temperatures, the designer looks to more refractory materials, often ceramics. Uranium dioxide (UO_2) is currently being used or tested for use in a number of reactors.[1,2,3] Primarily used as a dispersed phase in a ceramic or metal matrix, it is relatively stable and chemically inert to matrix and cladding materials. The melting point of UO_2 is in excess of 2700° C, which is more than twice that of the metal. A number of other uranium oxides are reported[4] (UO, U_4O_9, U_2O_5, U_3O_7, U_3O_8 and UO_3), but their instability make them unsuitable for use in fuel elements. Although UO_2 oxidizes upon heating in an air of oxygen atmosphere, this difficulty has been overcome by processing in an inert atmosphere.[2]

Investigations now being made to determine the suitability of the carbides, nitrides and silicides have as their principal objective a refractory material with a higher uranium concentration. This may be expressed as weight percent uranium or as weight of uranium per unit volume of compound (g/cm^3). Table I shows a comparison of some of these materials.

J. I. Mueller

The ThO_2-UO_2 system has been under investigation as a fuel element possibility in fast breeder reactors. This system is highly refractory and stable under normal operating conditions. Mixtures up to 10 weight percent UO_2 have been found satisfactory.[7] The low thermal conductivity of these bodies was deemed satisfactory for a boiling water reactor since its conditions would bring about a uniform heat transfer between the fuel element and the coolant. The thermal cycling of a reactor would, however, tend to cause extreme thermal shock, resulting in cracking of the mixture. Some studies have been made on the system UO_2-PuO_2, again for use as breeder fuels. Both the UO_2-ThO_2 and UO_2-PuO_2 systems for solid-solution series are more stable in air at high temperatures than the UO_2 elements.

A number of ceramic materials have been under consideration as either additives or as a matrix material. Among others, these include aluminum oxide, (Al_2O_3),[8] beryllium oxide (BeO),[9] cerium oxide (CeO),[8] lanthanum oxide (La_2O_3),[10] silicon carbide (SiC),[11] yttrium oxide (Y_2O_3),[12] and zirconium oxide (ZrO_2).[13] In general these materials are being considered for their stabilizing effects or their high heat transfer.

Moderators and Reflectors

The function of the moderator is to reduce the energy level of neutrons from the "fission level" to

TABLE I[5,6]

PROPERTIES OF SOME URANIUM COMPOUNDS

Compound	Melting Point (°C)	Theoretical Density (g/cm^3)	Uranium (g/cm^3)	Content w/(%)
UC	2375	13.63	12.97	91.3
UC_2	2475	11.68	10.61	87
UN	2630	14.32	13.50	90.5
U_3Si	930	15.58	14.99	96.2
USi_2	*ca.* 1600	9.25	7.48	85.8
UO_2	2878	10.96	9.66	84.5

TABLE II[6]

COMPARISON OF PROPERTIES OF BERYLLIUM OXIDE AND CARBIDE

Compound	Melting Pt. (°C)	Bulk Density (g/cm^3)	Thermal Neutron Cross-Sec. (cm^2/cm^3)	Thermal Conductivity (g-cal/sec/ cm^2/°C/cm)	Coeff. Thermal Expansion (10^6/°C)
BeO	2350±30	2.86	0.00074	0.500 (100°C)	45 (20°C)
Be_2C	Decomp. 2100	2.44	0.0010	0.056 (20°C)	10.8 (38-9820°C)

TABLE III

PROPERTIES OF CERAMIC MATERIALS CONSIDERED FOR CONTROL ELEMENTS

Compound	Melting Pt. (°C)	Density (g/cm^3)	Thermal Neutron Cross-Sec. (cm^2/cm^3)	Thermal Conductivity (g-cal/sec/ cm^2/°C/cm)	Coeff. Thermal Expansion (10^6/°C)
Gd_2O_3	2350±20	7.4	1090	0.005 (1000)	10.5 (25-1000)
Sm_2O_3	2350±20	7.43	167	0.004 (1000)	9.9 (25-1000)
B_4C	2450	2.51	82	0.065 (20)	4.5 (25-800)
BN	*ca.* 2750	2.25	60	0.065[a] (700) 0.032[b] (700)	0.77 (20-865) 7.51 (20-865)
HfO_2	2900±25	9.68	3	....	5.8 (250-1300)

[a] Perpendicular to pressing direction.
[b] Parallel to pressing direction.

the "thermal level." Moderator materials, therefore, must have high scattering cross sections, a large energy loss per collision, and a low absorption cross section. Reflectors, whose prime function is to reflect or scatter neutrons back into the core, require materials with the same general properties as those used as moderators. The substances which are generally considered satisfactory for these are ordinary and heavy water, graphite, and beryllium as a metal, oxide, or carbide.

Graphite is currently the most widely used material for these purposes. It is readily available, has relatively low cost, is thermally stable, and for the most part has satisfactory mechanical properties. Allowances must be made for changes in physical properties due to neutron damage. These include a sharp decrease in thermal conductivity, dimensional unstability, hardening, and the storage of large quantities of energy which can be released as heat.[14] Another disadvantage of graphite is its oxidation at high temperatures.

Beryllium has the nuclear properties necessary to make it an ideal material for use as a moderator or reflector. Beryllium oxide is of interest both because of its low absorption cross section and its refractoriness and thermal conductivity. Its principal disadvantages are the attack by water vapors at elevated temperatures and its toxicity. The latter necessitates extreme care in its use, usually complete containment. This requirement increases the problems of fabrication and sintering but is of no greater magnitude than those encountered in working with enriched fuels. Specimens of high densities (85-95 per cent theoretical) have been formed by hot pressing or by hydrostatic pressing and high-temperature sintering. These high density, low porosity materials have been found to have satisfactory resistance to attack by liquid sodium at temperatures up to 1500° F.[15] Beryllium carbide is also very refractory and has a low cross section (Table II), but it is difficult to produce and the problems of fabrication exceed those of the oxide. Since the properties of the carbide are so similar to those of the oxide, the latter is the preferred material.

In addition to the above materials, considerable interest is being evidenced in the development of hydride moderators. The principal work is centered on the zirconium hydride and the niobium hydride systems. To date, most of the work has been to determine the physical, mechanical, and chemical properties of the two materials.[16,17]

Control Devices

The control of the fission reaction in a reactor may be accomplished in a number of ways. One method is to use rods made up of materials with high absorption cross sections for thermal neutrons. These are inserted or removed from the core in such a manner as to decrease or increase the neutron flux in the core. The materials used in these control rods, in addition to the high cross section, must have stability with respect to heat and radiation, adequate strength, and a high coefficient of conductivity. Principal ceramic materials considered for use in control elements are shown in Table III.

Because of the extreme thermal shock to which the control rods are exposed, most of the ceramics in current use for this purpose are dispersion materials. Typical examples of these are *Boral* (B_4C in aluminum) and the carbides and oxides of the rare earths in stainless steels. However, work is continuing in an attempt to get a higher-temperature resistant material with the other necessary properties.[18]

Shielding

The purpose of shielding is to absorb all forms of incident energy and to emit only heat energy. Since a broad spectrum of energies must be considered, shielding materials can be classified in three ways:

1. Heavy elements for the absorption of gamma rays and the deacceleration of neutrons.
2. Moderator materials to slow down thermal neutrons.
3. Materials which will absorb neutrons and not emit short wave length radiation.

Lead has been used as a heavy element shield owing to its availability, low cost, absorption cross section, and ease in forming. The low melting point of this element is a distinct disadvantage. Tantalum and tungsten both have much higher melting points and nearly equivalent shielding value but both are expensive and subject to oxidation at elevated temperatures. At present, consideration is being given to the borides, carbides, and nitrides of the heavy elements. Most of these are quite refractory and can be readily produced. The forming of intricate parts offers the greatest problem here. Carbides and borides are being thoroughly studied as shielding materials for the third category above.

One group of ceramic materials which have become practically indispensable in the nuclear field are the high lead content glasses. These materials are of optical grade, having a 98 per cent transmission per inch in the visible region. They are extremely dense (6.2 g/cc) and have an absorption equivalent of 0.55 of Pb, 1.0 of steel, and 3.0 of concrete. These are used as windows in junior caves, hot cells, and in low energy areas of reactors.

Advantages and Disadvantages of Ceramics

The most obvious advantage gained in using ceramic materials is their resistance to high temperatures. The oxides and carbides of most metals are generally more refractory than the metal. Not only do ceramics wtihstand higher temperatures but many retain all but a small percentage of their room-temperature strengths. That ceramic materials have some of the highest compressive strengths is recognized, but at the same time their low tensile strengths often limit areas of use. The lower conductivities of thermal expansion exhibited by ceramics is often desirable for insulating properties, but when a material has a high thermal expansion and low conductivity, its resistance to heat absorption is often poor. This must be considered in the use of ceramics for reactors since extreme temperature excursions may be the rule rather than the exception. As indicated, a number of ceramic materials have properties which fall within a satisfactory range. The intended use, weight, or strength-to-weight ratio may be an important consideration. Again the ceramic materials' lower density may be a factor to be considered.

One distinct disadvantage of ceramics has been the difficulty encountered in the processing (forming, and sintering) of the desired shape. Two or more distinct processes are generally required in even simple shapes. Modern technology, however, has so developed the art of hot pressing, hydrostatic pressing, rolling and sintering that future practices may be more reliable and less complex. Ceramic materials with extreme dimensional tolerance are now being manufactured, thus overcoming one previous deterent.

When a crystalline material undergoes radiation, two general effects can occur: displacement of the atoms from their normal lattice sites (Frenkel defects) and ionization of the atoms, both resulting in the formation of lattice defects. (The first process is more common in metals and the second in non-metals.) The chemical and physical properties of these materials will be affected by these lattice defects.

The effect of radiation on non-metals may be classed into three major areas: structural effects, electronic effects, and diffusion controlled rate process effects. Local strain and distortion caused by lattice defects seriously affect structure-sensitive properties. The movement of lattice defects results in diffusion in the solid; thus, since irradiation increases the amount of these defects, the diffusion rate is increased.

In considering radiation stability of materials, the formation and stability of materials under operating conditions is a function of crystal structure and bonding. The materials which have high symmetry and possess ionic bonding are considered more stable than those possessing covalent bonding. The latter, on the other hand, are less susceptible to damage than solids with metallic bonding. Radiation damage in ionic crystals can be overcome by heat effects,[19] since the crystals are self-annealed at elevated temperatures. Inasmuch as many ceramic materials exhibit bonds that are primarily ionic in character, their properties will not be affected by radiation at service temperatures.

It can be concluded, then, that the materials problem in a reactor design can be assisted by the judicious use or consideration of the proper ceramic

materials. Of prime consideration here is the recognition of ceramic materials *as a whole*—a group of substances whose preparation, properties, and reactions are often quite dissimilar to those of metals and plastics. For this reason, attempts to describe the use of ceramics in the terms and connotations applied to other materials are often unsuccessful and fail to convey a sense of the important part which ceramics can play in the reactor field.

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Engineering Research Dividends

Gomez, M. P., "A Study of the Decomposition of the Alpha Prime Phase of the System Titanium-Copper." M.S. in Metallurgical Engineering, 1959.

It was the object of this investigation to follow and interpret the kinetics of the decomposition of martensite in a Ti-7%Cu alloy during tempering. A knowledge of this reaction, though of no direct practical bearing, may help future investigators searching for fundamental data on the subject. As a by-product, the author obtained information that will help to clarify the controversy developed from previous work concerning the intermetallic compounds Ti_3Cu and Ti_2Cu. The method used in following the reaction kinetics of the transformation of the Ti-7%Cu martensite involved precise measurements of the electrical resistance of specially prepared and treated rods of the alloy. Metallographic and X-ray diffraction studies of powders and lumps were used to identify the phases present. From this two-part investigation, the writer drew the following conclusions:

1) The phase in equilibrium with alpha at room temperature is Ti_2Cu. Ti_3Cu was not found even in metastable equilibrium. Though no special efforts were made to determine the crystallographic structure of Ti_2Cu, some evidence was found that it is not FCC as previously reported.

2) The data justified the conclusion that up to 60% transformation the tempering of the alpha prime phase has the characteristics of a log autocatalytic reaction. Beyond that point a Cohen type of equation represents the transformation more closely, especially at higher temperatures.

Kamdar, M. H., "Quantitative Determination of Glassy Phase in High Alumina Bodies," M.S. in Ceramic Engineering, 1958.

Many ceramic materials utilize a glassy phase as a bond; however, in certain applications, the presence of appreciable amounts of glass may be a detriment. Among these are those aluminum oxide bodies used as a dielectric. Quantitative determinations of the glass present were made by microscopic, chemical and X-ray diffraction methods.

A procedure was developed whereby the amount of glass present could be determined by X-ray diffraction with one per cent accuracy. These results were coordinated with those obtained by chemical leaching. The use of the X-ray technique permits a rapid analysis which would be of use in either research or production control.

Hodson, J. Turnbaugh, "Dental Ceramics," M.S. in Ceramics, 1958.

Porcelain is one of the materials used for dental restorations. Although porcelain restorations have been effectively used for many years, few quantitative data have been published on the properties of the porcelains. This study was made on porcelains secured on the open market in the form used by dentists. Established engineering testing methods were

followed except that specimens were generally smaller, to conform with the small size of dental restorations. Dental techniques in forming and firing were reviewed and clinical considerations were mentioned. The phase compositions of twelve porcelains were analyzed under the petrographic microscope. Three representative porcelains (Dentsply, Steele's and S. S. White) were then tested for transverse strength, firing shrinkage, specific gravity, and porosity.

The porcelain powders were composed primarily of frits and feldspars. These mixtures result in highly vitreous fired restorations which have the translucence and coloring of natural teeth. The disadvantage of this material lies in its brittleness and in the exacting technical procedures necessary for its fabrication. However, vitreous porcelain remains the best dental restorative material combining permanence and esthetics in replacing lost tooth structure.

Some of the results of this study appeared in *Am. Cer. Soc. Bull.*, Vol. 36, No. 8, "A Preliminary Study of Dental Porcelains" and in *Jour. Prosthetic Dentistry*, Vol. 9, No. 2, "Some Physical Properties of Three Dental Porcelains."

GRADUATE STUDIES AND RESEARCH

(Continued from page 7)

carried out to determine if greater advantage can be taken of this mechanism by using deeper bubble columns. The investigation is continuing.

PROJECT: Investigation of the resistance encountered by heavy specific gravity particles settling through a fluid mineral suspension

GRADUATE STUDENT: Luis B. Alcid

The resistance offered to solid particles moving in pure liquids is explained by the laws of Newton and Stokes under conditions of turbulent and laminar flow, respectively. In mineral suspensions additional resistance forces are offered to penetration which have not been well defined. This investigation initially developed an apparatus which could be used in measuring the rate of penetration of heavy particles through suspensions. At present data are being gathered in an effort to isolate and identify numerous factors contributing to hindered settling conditions.

ANALYSIS OF A SLAG-METAL SYSTEM

(Continued from page 27)

The holder shown in Fig. 2-b can be used to run rapid analysis for copper in both a Cu-Pb alloy and a PbO-SiO_2-Cu_2O slag. More precautions are required for the ternary slags than the binary alloys because of the difference in the physical condition of the standard slags, which are fine crystalline materials, and that of the unknown slags, which are dense glassy materials.

FLOTATION OF CHROMITE FROM OLIVINE

(Continued from page 12)

cations to cause extensive depletion of useful fatty acid by formation of soap molecules in solution. The evidence indicated that such was the case in the absence of fluoride, and that it occurred to the extent that insufficient collector was available for adequate promotion of the chromite. Both the fluoride and the hydroxyl ion have similar ion radii (2.7A), and their respective iron and magnesium precipitates have similar degrees of insolubility. The metal oleates form at pH values close to the hydroxides. However, the experimental pulp behavior favored the explanation that sufficient iron and magnesium was withdrawn as insoluble fluoride during the grinding stage to allow a suitable concentration of active collector to be present for the collection of chromite.

Table III indicates the final results of the flotation procedure; assays were by chemical analysis. A recovery of 93.0 per cent of the Cr_2O_3 was effected in the cleaner concentrate at a grade of 47.41 per cent Cr_2O_3 and Cr-to-Fe ratio of 2.32. The rougher tailing contained 3.6 per cent of the Cr_2O_3 at a grade of 2.02 per cent Cr_2O_3.

Figure 17 shows the appearance of the mineralized froth in the rougher flotation stage. The intense degree of collection is evidenced by the heavily-loaded froth column. The armored shells of chromite particles are detectable in the lower part of the column, while some indication of the selectivity is given by the difference in appearance between the column and the solids residing at the bottom of the flotation cell.

This investigation developed a very selective technique for chromite flotation from a refractory ore. Although further testing is required to confirm specific mechanisms, a contribution has been made to the understanding of reagent functions in nonmetallic flotation.

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